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OCCUPATIONAL EXPOSURE

TO

AMMONIA

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
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1974

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PREFACE

The Occupational Safety and Health Act of 1970 emphasizes the need for standards to protect the health and safety of workers exposed to an ever-increasing number of potential hazards at their workplace. To provide relevant data from which valid criteria and effective standards can be deduced, the National Institute for Occupational Safety and Health has projected a formal system of research, with priorities determined on the basis of specified indices.

It is intended to present successive reports as research and epidemiologic studies are completed and sampling and analytic methods are developed. Criteria and standards will be reviewed periodically to ensure continuing protection of the worker.

I am pleased to acknowledge the contributions to this report on ammonia by members of my staff, by the Review Consultants on Ammonia, by the ad hoc committee of the Industrial Medical Association, by Robert B. O'Connor, M.D., NIOSH consultant in occupational medicine, and by Edwin C. Hyatt, NIOSH consultant on respiratory protection. The NIOSH recommendations for standards are not necessarily a consensus of all the consultants and professional societies that reviewed this criteria document on ammonia. Lists of the NIOSH Review Committee members and of the Review Consultants appear on the following pages.

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The Office of Research and Standards Development, National Institute for Occupational Safety and Health, had primary responsibility for development of the criteria and recommended standard for ammonia. The University of Washington School of Public Health and Community Medicine developed the basic information for consideration by NIOSH staff and consultants under contract No HSM-99-73-36. Bryan D. Hardin had NIOSH program responsibility and served as criteria manager.

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CRITERIA DOCUMENT: RECOMMENDATIONS FOR AN OCCUPATIONAL EXPOSURE STANDARD FOR AMMONIA

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I. RECOMMENDATIONS FOR AN AMMONIA STANDARD

The National Institute for Occupational Safety and Health (NIOSH) recommends that worker exposure to ammonia be controlled by requiring compliance with the following sections. The standard is designed to protect the health and safety of workers for a 40-hour workweek over a working lifetime. Compliance with all sections of the standard should prevent adverse effects of exposure to ammonia in the workplace air. The standard is measurable by techniques that are valid, reproducible, and available to industry and government agencies. Sufficient technology exists to permit compliance with the recommended standard. The standard will be subject to review and revision as necessary.

"Ammonia" is defined as gaseous or liquified anhydrous ammonia and aqueous solutions thereof (aqua ammonia, ammonium hydroxide). "Strong aqua ammonia" is defined as aqueous solutions containing more than 10% ammonia. "Weak aqua ammonia" is defined as solutions of 10% or less.

Section 1 - Environmental (Workplace Air)

(a) Concentration

Occupational exposure shall be controlled so that no worker is exposed to ammonia at greater than a ceiling concentration of 50 ppm as determined by a 5-minute sampling period.

(b) Sampling and Analysis

Procedures for sampling, calibration of equipment, and analysis of ammonia samples shall be as provided in Appendices I and II, or by any method shown to be equivalent in precision, accuracy, and sensitivity to the methods specified.

Section 2 - Medical

(a) Preplacement medical examinations shall be made available for all workers whose employment may involve potential exposure to ammonia concentrations in excess of 50 ppm. The examination shall be directed toward, but not limited, to the eyes, skin, and upper respiratory system. Pulmonary function tests should be carried out at the time of the preplacement examination. An evaluation of the advisability of the worker's using negative or positive pressure respirators shall be made.

(b) Medical surveillance shall be made available for all workers in whose eyes liquid ammonia has been splashed, who have signs and symptoms of eye irritation after exposure to ammonia, who exhibit signs or symptoms of respiratory tract (throat, trachea, lungs) irritation caused by ammonia exposure, or who experience skin irritation as a result of ammonia exposure.

(c) Initial examinations for presently employed workers shall be made available within 6 months of the promulgation of a standard incorporating these recommendations.

(d) Records of preplacement medical examinations and of required medical surveillance shall be maintained for the period of employment. The medical representatives of the Secretary of Health, Education, and Welfare, of the Secretary of Labor, of the employer, and of the employee shall have access to all medical records.

Section 3 - Labeling (Posting)

(a) Containers of anhydrous ammonia shall be marked in accordance with 29 CFR 1910.111 as amended and shall bear the following label in addition to or in combination with labels required by other statutes, regulations, or ordinances:

AMMONIA, ANHYDROUS

DANGER! HAZARDOUS LIQUID AND GAS

LIQUID CAUSES BURNS

GAS EXTREMELY IRRITATING

Do not breathe gas

Do not get in eyes, on skin, on clothing

In case of exposure, evacuate to fresh air

In case of contact, immediately flush skin or eyes with plenty of water for at least 15 minutes. Get medical attention at once in case of eye contact or burns to the nose or throat, or if the patient is unconscious.

CYLINDER HANDLING AND STORAGE

Keep away from heat

Never drop cylinders

Be sure connections are tight

Loosen closure carefully

Never refill cylinders. ICC Regulations prohibit refilling without permission of owner.

Have airline respirator or self-contained breathing apparatus available for emergency

(b) Containers of strong aqua ammonia (greater than 10%) shall bear the following label in addition to or in combination with labels required by other statutes, regulations, or ordinances:

AMMONIUM HYDROXIDE (STRONG AQUA AMMONIA)

WARNING! LIQUID CAUSES BURNS

GAS EXTREMELY IRRITATING

Avoid breathing gas

Avoid contact with eyes, skin, and clothing

In case of contact, immediately flush skin or eyes with plenty of water for at least 15 minutes; for eyes, get medical attention

HANDLING AND STORAGE

Before moving containers, be sure closure is securely fastened

Avoid rough handling or dropping

Loosen closure carefully

Keep out of sun and away from heat

Completely drain container before returning to supplier

In case of spillage, flush with plenty of water

(c) Containers of weak aqua ammonia (10% or less) shall bear the following label in addition to or in combination with labels required by other statutes, regulations, or ordinances:

AMMONIUM HYDROXIDE (AQUA AMMONIA)

CAUTION! IRRITATING LIQUID AND GAS

Loosen closure carefully

Avoid breathing gas

Avoid contact with eyes, skin, and clothing

In case of contact, immediately flush skin or eyes with plenty of water for at least 15 minutes; for eyes, get medical attention

In case of spillage, flush with plenty of water

(d) The following warning sign shall be affixed in a readily visible location at or near entrances to areas containing anhydrous or strong aqua ammonia and in which there is a reasonable potential for emergencies. This sign shall be printed both in English and in the predominant language of non-English-speaking workers, unless they are otherwise trained and informed of the hazardous areas. All illiterate workers shall receive such training.

WARNING!

AMMONIA HAZARD AREA

UNAUTHORIZED PERSONS KEEP OUT

In emergency, do not enter unless wearing respiratory, eye, and skin protection.

CAUSES BURNS--SEVERE EYE HAZARD

INHALATION OF HIGH CONCENTRATIONS MAY BE FATAL

GAS MASKS LOCATED AT (specific locations to be supplied by employer)

(e) All anhydrous ammonia systems, piping, and associated equipment shall comply with 29 CFR 1910.111, as amended. Shut-off valves of all ammonia systems shall be conspicuously labeled.

Section 4 - Personal Protective Equipment

(a) Protective Clothing

(1) Personnel handling anhydrous or strong aqua ammonia where skin or eye contact is likely to occur shall wear gloves, shoe covers, and aprons impervious to ammonia. Unless eye and face protection is afforded by a respirator hood or facepiece, chemical goggles and face shields shall be worn. Eye and face protective equipment and its use shall conform to 29 CFR 1910.133, as amended.

(2) In addition to the respiratory protection specified in Table I-1, personnel required to enter atmospheric ammonia concentrations likely to be more than 10,000 ppm shall wear, under an impervious full body suit, a self-contained breathing apparatus with a positive pressure in a full facepiece or a combination supplied air impervious suit, continuous flow type, with auxiliary self-contained air supply. When the worker is using the impervious suit over a self-contained breathing apparatus, stay time in the area shall be limited with due consideration to the heat stress factors involved.

(3) The employer shall supply and maintain all protective clothing in a clean, sanitary, and workable condition.

(b) Respiratory Protection

The employer shall provide appropriate respirators and ensure proper use when a variance has been granted under the provisions of the Occupational Safety and Health Act to allow respirators as a means of control of exposure in routine operations, while the application for variance is pending, or whenever atmospheric concentrations of ammonia exceed 50 ppm, eg, for nonroutine operations, for occasional brief concentrations above the ceiling, cr for emergencies. For these instances a variance is not required, but the requirements set forth below continue to apply. Appropriate respirators as described in Table I-1 shall only be used pursuant to the following requirements:

(1) For the purpose of determining the type of respirator to be used, the employer shall measure the atmospheric concentration of ammonia in the workplace when the initial application for variance is made and thereafter whenever process, worksite, climate, or control changes occur which are likely to increase the ammonia concentration; this requirement shall not apply when only atmosphere-supplying positive pressure respirators are used. The employer shall ensure that no worker is being exposed to ammonia in excess of the standard because of improper respirator selection, fit, use, or maintenance.

(2) A respiratory protective program meeting the requirements of 29 CFR 1910.134 as amended shall be established and enforced by the employer.

(3) The employer shall provide respirators in accordance with Table I-1 and shall ensure that when required by circumstances the employee uses the respirator provided.

(4) Each area required to be posted in accordance with Section 3(d) shall have emergency respiratory protection readily available

TABLE I-1
RESPIRATOR SELECTION GUIDE FOR PROTECTION AGAINST AMMONIA

Multiples of Ceiling	Respirator Type
Less than or equal to 2X	1) Chemical cartridge respirator with replaceable ammonia cartridge and half mask facepiece; or 2) Type C supplied air respirator, demand type (negative pressure), with half mask facepiece.
Less than or equal to 20X	Fullface gas mask, chin type, with ammonia canister.*
Less than or equal to 50X	1) Fullface gas mask, chest or back mounted type, with industrial size ammonia canister;** or 2) Type C supplied air respirator, demand or pressure demand type (negative or positive pressure), with full facepiece, hood, or helmet with shroud.
Greater than 50X	1) Self-contained breathing apparatus with positive pressure in full facepiece; or 2) Combination supplied air respirator, pressure demand type, with auxiliary self-contained air supply.
Emergency (no concentration limit)	1) Self-contained breathing apparatus with positive pressure in full facepiece; 2) Combination supplied air respirator, pressure demand type, with auxiliary self-contained air supply; or 3) Fullface gas mask, back or front mounted type, with industrial size ammonia canister. Not for use in limited egress emergencies.
Evacuation or Escape (no concentration limit)	1) Self-contained breathing apparatus in demand or pressure demand mode (negative or positive pressure); 2) Fullface gas mask, front or back mounted type, with industrial size ammonia canister; or 3) Mouthpiece respirator with escape type ammonia canister (escape type gas mask).

* Maximum service life of 1 hour only.
** Maximum service life of 2 hours only.

in nearby locations which do not require entry into a contaminated atmosphere for access. Such respiratory protection shall consist of:

(A) Outdoor areas: At least 2 fullface gas masks, chest or back mounted type, with industrial size ammonia canisters (maximum life 2 hours).

(B) Indoor areas requiring worker entry to control spills or leaking tanks: At least 2 fullface gas masks, chest or back mounted type, with industrial size ammonia canisters.

(C) Indoor or outdoor confined spaces with limited egress, such as tanks, pits, etc, requiring worker entry: At least 2 self-contained breathing apparatus, pressure demand type (positive pressure). In addition, see Work Practices requirements in Section 6(f)(2).

(5) Respiratory protective devices described in Table I-1 shall be those approved under the provisions of 30 CFR 11, published in the Federal Register, March 25, 1972, as amended.

(6) Respirators specified for use in higher concentrations of ammonia may be used in atmospheres of lower concentrations.

(7) The employer shall ensure that respirators are adequately cleaned, maintained, and stored when not in use, and that employees are instructed on the use of respirators assigned to them and on testing for leakage.

(8) Canisters shall be discarded and replaced with fresh canisters after use. Unused canisters shall be discarded and replaced when the seal is broken, after 3 years if seals are unbroken, or on the manufacturer's recommendation, whichever is first.

Section 5 - Informing Employees of Hazards from Ammonia

At the beginning of employment, workers whose jobs may involve exposure to concentrations greater than 50 ppm, or who will work in areas required to be posted in accordance with Section 3(d), shall be informed of the hazards, relevant symptoms of overexposure, appropriate emergency procedures, and precautions to ensure safe use and to minimize exposure. First aid procedures will be included, with emphasis on the importance of prompt, copious irrigation of the eyes despite the initial lack of pain. The information shall be posted in the work area, and kept on file, readily accessible to the worker at all places of employment where ammonia is involved in unit processes and operations, or is released as a product, byproduct, or contaminant.

A continuing educational program shall be instituted to ensure that all workers have current knowledge of job hazards, first aid procedures, proper maintenance procedures and cleanup methods, and that they know how to correctly use respiratory protective equipment and protective clothing. Retention of this information by workers in areas required to be posted in accordance with Section 3(d) shall be verified by drills simulating potential emergency situations appropriate to the work situation, held at intervals not exceeding 6 months. Drills should cover, but not be limited to, the following:

Evacuation procedures

Handling of spills and leaks, including decontamination

Location and use of emergency firefighting equipment

First aid and rescue procedures

Use of protective clothing and location, use, and care of respiratory protective equipment

Location and use of shut-off valves

Location, purpose, and use of safety showers, eye wash fountains, and other sources of water for emergency use

Operating procedures

Entry procedures for confined spaces

Prearranged procedures for obtaining emergency medical care.

Deficiences noted during the drill shall form the basis for a continuing educational program to ensure that all workers have current knowledge. Records of drills and training conducted shall be kept and made available for inspection by authorized personnel as required.

Information as required shall be recorded on US Department of Labor Form OSHA-20 "Material Safety Data Sheet" or a similar form approved by the Occupational Safety and Health Administration, US Department of Labor.

Section 6 - Work Practices

(a) Emergency Procedures

For all work areas in which there is a reasonable potential for emergencies, procedures as specified below, as well as any other procedures appropriate for a specific operation or process, shall be formulated in advance and employees shall be instructed in their implementation.

(1) Procedures shall include prearranged plans for obtaining emergency medical care and for necessary transportation of injured workers.

(2) Approved eye, skin, and respiratory protection as specified in Section 4 shall be used by personnel essential to emergency operations.

(3) Nonessential employees shall be evacuated from exposure areas during emergencies. Perimeters of areas of hazardous exposures shall be delineated, posted, and secured.

(4) Personnel shall keep upwind of spills or leaks if possible. Personnel properly trained in the procedures and adequately protected against the attendant hazards shall shut off sources of ammonia, clean up spills, and immediately repair leaks.

(5) Water sprays to absorb ammonia gas or to dilute aqua ammonia shall be used as needed. Water used to absorb ammonia shall not be discharged to municipal or confined sewers unless adequately diluted or otherwise treated to meet applicable local, state, or federal discharge and water pollution regulations. Water should not be used on large spills of liquid anhydrous ammonia because heat generated may increase volatilization of the ammonia with consequent increase of exposure.

(6) In case of fire, ammonia sources shall be shut off or removed. Containers shall be cooled with water spray. Chemical foam or dry chemicals shall be used for fighting anhydrous ammonia fires, and proper respiratory protection and protective clothing shall be worn.

(b) Control of Airborne Ammonia

(1) Engineering controls such as process enclosure or local exhaust ventilation shall be used to maintain ammonia concentrations within the limits of the recommended standard. Ventilation systems shall be designed to prevent the accumulation or recirculation of ammonia in the

workroom and to effectively remove ammonia from the breathing zones of workmen. Exhaust ventilation systems discharging to outside air must conform with applicable local, state, and federal air pollution regulations. Ventilation systems shall be subject to regular preventive maintenance and cleaning to ensure maximum effectiveness, which shall be verified by periodic airflow measurements.

(2) General ventilation may be used to reduce room concentrations of ammonia if worker exposure is not increased thereby.

(c) Storage

(1) Anhydrous ammonia shall be stored in accordance with the provisions of 29 CFR 1910.111, as amended.

(2) Strong aqua ammonia shall be stored in:

(A) Cool, dry, well ventilated areas located outside buildings or in sections especially provided for ammonia.

(B) Areas free from oxidizers and sources of ignition. Due consideration shall be given to health and fire hazards, population density, and proximity of water supplies when locating ammonia storage areas.

(C) Containers which are protected from heat, corrosion, and mechanical damage.

(D) Closed containers which are provided with safety relief valves as necessary.

(d) Waste Disposal

(1) Disposal of waste ammonia shall conform to all applicable local, state, and federal regulations. Rapid neutralization of large amounts of ammonia, or addition of water to liquid anhydrous ammonia is not

desirable because the heat generated may increase exposure of personnel. If regulations permit, spills shall be diluted with water, carefully neutralized, and discharged to the sewer with a large excess of water.

(2) Any discharges of ammonia to the atmosphere shall be controlled to prevent injury.

(e) General Work Practices

(1) Written operating instructions and emergency medical procedures shall be formulated and posted where ammonia is handled or used.

(2) Contact lenses should not be worn when working with ammonia.

(3) Ammonia should never be mixed with chlorine bleach. To do so releases the hazardous gas chloramine.

(4) Metals other than iron or steel should not be used in contact with ammonia.

(5) Containers and systems shall be handled and opened with care to avoid sudden release of pressure. Approved eye and respiratory protection shall be worn while opening, connecting, or disconnecting ammonia containers and systems. When opening containers and systems, adequate ventilation shall be available to remove inadvertent discharges of ammonia.

(6) Containers and systems shall be frequently inspected for leaks. All ammonia equipment including hose fittings and connections shall be inspected frequently for tightness and good working order. Needed repairs and adjustments shall be promptly made.

(7) Workers should stand upwind when transferring ammonia and in a position from which the operation can be controlled. Workers

should not stand in direct line of any valve or fitting opening, particularly the openings of safety relief valves, in order to avoid being sprayed with ammonia.

(8) Inadvertent entry of ammonia into disconnected containers and systems while work is in progress shall be prevented by blanking off ammonia supply lines.

(9) Work areas where ammonia is handled or used shall be equipped with sources of water. Permanent installations shall have eye wash fountains and safety showers. Hoses shall be available for washing down spills and decontaminating surfaces where applicable.

(10) Mobile operations involving handling of anhydrous or strong aqua ammonia shall have at least 5 gallons of clean, fresh water available in a readily accessible container. If necessary, these containers shall be protected from freezing by insulation or by an external source of heat. More than 5 gallons may be needed based on the number of workers or their dispersion. A means of utilizing this water for flushing eyes and skin, such as a dipper or squeeze bottle, shall be available.

(11) Unauthorized personnel shall not be permitted to enter areas required to be posted in accordance with Section 3(d).

(12) Work areas shall be kept clean and orderly. Accesses to ammonia shut-off valves shall be kept unobstructed. Shut-off valves shall be conspicuously marked.

(f) Work Practices for Specific Operations or Areas

The following is not intended to be a comprehensive or complete listing. It is presented to emphasize and clarify the requirements, in addition to those listed under General Work Practices, for the following operations or areas.

(1) Ammonia Hazard Areas

Exits from areas required to be posted in accordance with Section 3(d) shall be plainly marked. Emergency exit doors shall be conveniently located and shall open into areas which will remain free of contamination in an emergency.

(2) Confined Spaces

(A) Tanks, pits, tank cars, process vessels, tunnels, sewers, etc, which have contained ammonia shall be thoroughly ventilated, tested for ammonia, and inspected prior to entry.

(B) Inadvertent entry of ammonia into the confined space while work is in progress inside shall be prevented by disconnecting and blanking off ammonia supply lines.

(C) Confined spaces shall be ventilated to keep any ammonia concentration below the standard and to prevent oxygen deficiency.

(D) Personnel entering confined spaces shall be equipped with a lifeline tended by another worker outside the space. The worker on the outside shall be equipped with approved respiratory, eye, and skin protection.

(E) Entry into confined spaces shall be controlled by a permit system. Permits shall be signed by an authorized employer representative certifying that preparation of the confined space, precautionary measures, personal protective equipment, and procedures to be used are all adequate.

(3) Enclosed Spaces

Enclosed spaces (rooms, buildings, etc) which ordinarily are safe to enter but which, due to the failure of a system inside, could contain hazardous concentrations of ammonia should have a continuous automatic monitor set to sound an alarm outside the enclosed space if ammonia concentrations exceed the recommended standard. If such areas are not monitored in this way, the enclosed space shall be entered only if the worker is under observation by a co-worker or if the worker has in his possession a respirator suitable for escape.

(4) Diazo-type Reproducing Operations

(A) Diazo-type reproducing equipment shall have mechanical local exhaust ventilation to control ammonia escaping from the machine, from the paper discharged from the machine, and during refilling of reservoirs with ammonia.

(B) Anhydrous or aqua ammonia containers should be stored outdoors or in ventilated rooms separate from the reproducing machine room.

(C) Approved protective clothing, eye and respiratory protection shall be used when handling ammonia, or connecting or disconnecting ammonia containers.

(5) Laboratories

Work with ammonia in laboratories shall take place in properly designed and functioning laboratory hoods. Approved eye and skin protection should be worn while handling ammonia.

(6) Nitriding Furnaces

Exhaust ventilation shall be installed over the vent.

(7) Agricultural Operations

(A) Farm vehicles for transporting ammonia shall conform to the provisions of 29 CFR 1910.111, as amended.

(B) When manipulating or adjusting ammonia dispensing equipment or when working in close proximity to it (for example, see (E) and (G), below), agricultural workers shall use approved chemical goggles or face shields, and gloves impervious to ammonia.

(C) Individual plastic squeeze bottles holding at least 8 ounces of water shall be carried by each worker for flushing ammonia from eyes without delay.

(D) For washing ammonia from eyes and skin, at least 5 gallons of clean, potable water shall be carried with all fertilizer nurse and applicator tanks. The container shall be checked daily and be protected as necessary from freezing by insulation or by an external source of heat. A dipper or other means of utilizing the water shall be carried.

(E) All ammonia equipment including hose fittings and connections shall be checked frequently for tightness and good working order.

(F) Farm workers shall be thoroughly indoctrinated in correct operating procedures before using ammonia equipment.

(G) Workers should stand upwind when transferring ammonia and in a position where the operation can be controlled. Workers should not stand in direct line of any valve or fitting opening, particularly the openings of safety relief valves, in order to avoid being sprayed with ammonia.

(H) Farm workers shall be alerted to the possible buildup of hazardous concentrations of ammonia gas in enclosed spaces from the biological decay of organic material such as manure. Barns, chicken houses, and similar buildings should be well ventilated.

Section 7 - Sanitation Practices

(a) It is most important that adequate supplies of clean water be available in areas where ammonia is handled or used. Speed is imperative in the removal of ammonia in contact with the eyes or skin by flushing with copious quantities of water.

(b) General plant housekeeping should be of a high order, assuring that escape routes and ammonia control equipment are kept clear. Plant sanitation shall meet the requirements of 29 CFR 1910.141, as amended.

Section 8 - Monitoring and Recordkeeping Requirements

Workroom areas shall be monitored for ammonia exposure if environmental levels, as determined on the basis of an industrial hygiene survey or by the judgment of a compliance officer, exceed half of the 5-minute ceiling of 50 ppm. Records of these surveys, including the basis for concluding that air levels are below 25 ppm, shall be maintained until a new survey is conducted. Surveys shall be repeated when any process change indicates a need for reevaluation or at the discretion of the compliance officer.

Requirements set forth below apply to areas in which there is exposure to 25 ppm or more. Employers shall maintain records of environmental exposures to ammonia based upon the following sampling and recording schedules:

(a) In all monitoring, samples representative of the exposure in the breathing zone of at least 25% of the employees in each operation or process shall be collected. Each worker shall be included in the sampling at least every 2 years.

(b) The first environmental sampling shall be completed within 6 months of the promulgation of a standard incorporating these recommendations.

(c) Environmental samples shall be taken as soon as possible, but no later than 30 days after first operation of a new process or process changes.

(d) Samples shall be collected at least semiannually in accordance with Appendix I for the evaluation of the work environment with respect to the recommended standard.

(e) Environmental monitoring of an operation or process shall be repeated at least weekly when the ammonia concentration has been found to exceed the recommended environmental standard. In such cases, suitable controls shall be initiated and monitoring shall continue at weekly intervals until 3 consecutive surveys indicate the adequacy of these controls. Monitoring need not be repeated at weekly intervals if the excessive exposure was the result of an unusual but readily identified and corrected cause such as a minor accidental spill. However, in such cases immediate action shall be taken to reduce exposure and to prevent a recurrence.

(f) Records of environmental measurements shall be maintained so that exposure information is available for individual employees and shall be maintained for the duration of that worker's employment. Records shall indicate the type of personal protective devices, if any, in use at the time of sampling. Each employee shall be able to obtain information on his own environmental exposure.

II. INTRODUCTION

This report presents the criteria and the recommended standard based thereon which were prepared to meet the need for preventing occupational diseases arising from exposure to ammonia. The criteria document fulfills the responsibility of the Secretary of Health, Education, and Welfare, under Section 20(a)(3) of the Occupational Safety and Health Act of 1970 to "...develop criteria dealing with toxic materials and harmful physical agents and substances which will describe...exposure levels at which no employee will suffer impaired health or functional capacities or diminished life expectancy as a result of his work experience."

The National Institute for Occupational Safety and Health (NIOSH), after a review of data and consultation with others, formalized a system for the development of criteria upon which standards can be established to protect the health of workers from exposure to hazardous chemical and physical agents.

Ammonia is a chemically simple compound with diverse properties that make it a widely used substance. It is a readily assimilated form of reduced nitrogen, so it is widely used as a fertilizer in the form of anhydrous or aqua ammonia or as the source of nitrogen for dry fertilizers; it has a boiling point of -33 C (-27 F) and is easily liquified, so it is useful in refrigeration systems; and it is a volatile alkali, thus useful for cleaning. Its alkaline properties make it a skin and eye irritant, but it is especially dangerous to the eyes because of its initially silent but subsequently blinding action. It is an annoying gas whose offensiveness can be readily confused with toxic effects. This offensiveness provides excellent warning properties, but perhaps has helped obscure proper attention to possible long-term toxic properties.

These criteria for a standard for ammonia are part of a continuing series of criteria developed by NIOSH. The proposed standard applies to the processing, manufacture, use of, or other occupational exposure to ammonia as applicable under the Occupational Safety and Health Act of 1970. The standard was not designed for the population-at-large, and any extrapolation beyond occupational exposures is not warranted. It is intended to (1) protect against injury from ammonia, (2) be measurable by techniques that are valid, reproducible, and available to industry and official agencies, and (3) be attainable with existing technology.

III. BIOLOGIC EFFECTS OF EXPOSURE

Extent of Exposure

At room temperature and pressure, ammonia is a colorless gas with a distinctive pungent odor. Its water solutions (aqua ammonia) emit ammonia gas. [1] Pertinent properties of ammonia are presented in Table XI-1. [1-3]

In terms of pounds produced each year, ammonia ranked second in 1971 and third in 1972 on a list of the top 50 chemicals produced in the United States. [4] Synthetic ammonia production has risen at an annual rate of 10-12% over the last two decades. [5,6] US production in 1950 was about 1.5 million tons, [6] rising to slightly over 14 million tons in 1971 and 1972. [4] Future annual growth rates were predicted to decline to 6-8%, leading to estimated consumptions of about 20 million tons in 1975 and 30 million tons in 1980. [5]

In 1971, ammonia was produced by approximately 80 companies in the US in as many as 100 separate plants. [6] About 80-85% of current production is used in fertilizer manufacture, with the remainder being taken by other industries. [5] Ammonia is used in a wide variety of industrial processes. A number of occupations with potential exposure to ammonia are listed in Table XI-2. [7-9]

NIOSH estimates that approximately half a million US workers have potential occupational exposure to ammonia.

Historical Reports

In 1859 Taylor [10] reported a number of poisonings after intentional or accidental ingestion of ammonia solutions. Patients experienced immediate, severe burning pain in the mouth, throat, and stomach which persisted in some cases up to 5 days. The ammonia reportedly "corroded and dissolved" tissues it contacted and caused severe local irritation. In 2 cases, ammonia was aspirated and the patients died as a result of lung damage. One case was cited in which the "vapor of strong ammonia" was applied to the nostrils of an epileptic who died 2 days later with what were described as symptoms of croup.

According to Horvath, [11] Lehmann in 1886 made the first important experiments on the effects of ammonia inhalation. Lehmann exposed himself for 30 minutes to ammonia at a concentration of 330 ppm and concluded that 300-500 ppm could be tolerated for a prolonged period. Horvath criticized the experiment for a number of reasons, including inaccuracies in the reported ammonia levels and the fact that the exposure was for only 30 minutes, and considered that Lehmann's conclusions were unjustified.

Effects on Humans

Ammonium ions are produced in the body as a protein metabolite. [12] Ammonium ions produced by deamination are rapidly converted in the liver into relatively harmless urea and excreted by the kidney or are used to make new amino acids. Ammonium ions are also produced in the kidney, conserving fixed base, thus maintaining electrolyte balance.

A. Odor Threshold

Available odor threshold data show a wide variation. Fieldner et al in 1921 [13] reported a threshold of 50 ppm in human exposure experiments. Smyth [14] found that 1 ppm was detected and identified by 10 subjects. Details of these experiments were not provided. Leonardos et al [15] used a panel of 4 trained odor analysts, each with more than 1 year of "analytical odor work." Exposures were made in a test room designed to minimize background odor. Ammonia was injected into the test room with a microsyringe and the resultant air concentration was computed based on the room volume. The threshold was taken as the lowest concentration at which the subject could define the odor, provided that he consistently recognized the odor at the next higher concentration. The authors did not report the lowest concentration detected or the threshold level for each test subject, but 46.8 ppm was reported as the lowest concentration which all 4 panel members could consistently recognize. Saifutdinov [16] found the odor threshold for ammonia for the most sensitive subjects in a group of 22 individuals to be 0.50-0.55 mg/cu m (approximately 0.6-0.7 ppm). No description of the method used was given. No data were found on the acclimatization of the odor threshold, but an industrial hygienist reported that "the sense of smell was quickly deadened to the presence of the gas" at a concentration of 9-37 ppm in an ice cream plant survey. [LD Pagnotto, written communication, September 1973]

B. Case Reports

In 1938 Slot [17] reported 6 cases of acute ammonia gas exposure following rupture of a pipe containing ammonia. Varying degrees of symptoms of acute inflammation of the respiratory tract and chemical skin burns were observed. Residual chronic bronchitis was evident in 2 cases. One worker died one month after the accident and the autopsy revealed acute laryngitis, tracheitis, bronchopneumonia, and pulmonary edema. The kidneys showed congestion and early hemorrhagic nephritis, which was attributed to toxemia secondary to chemical skin burns.

In 1941 Caplin [18] published a case report of 47 persons involved in a mass exposure to ammonia in a London air raid shelter when a connecting pipe of an ammonia condenser was ruptured. He divided the exposed individuals into groups depending on the extent of the respiratory involvement. The signs and symptoms ranged from mild upper respiratory irritation to inflammatory processes of the entire respiratory tract with complications of pulmonary edema and bronchopneumonia. The exposed individuals in Caplin's report were affected according to a clinical spectrum depending on their distance from the ammonia source and their time of exposure. Unfortunately, no air concentration estimates were given.

The 9 "mild" cases [18] exhibited only slight eye and upper respiratory irritation with hoarseness and tightness in the throat. They recovered quickly and were discharged from the hospital within a few hours. The 27 "moderately" affected individuals showed more pronounced upper respiratory irritation and, in addition, had a productive cough with tenacious, sometimes blood-stained sputum and moist rales in the lungs suggesting an extension of the inflammatory process into the lower respiratory tract. Three patients in this group developed pulmonary edema within 6 hours and died. Nine patients from the "moderate" group developed bronchopneumonia on the second and third days, and 3 of these died. The remaining 15 "moderately" affected persons made an uneventful recovery within one week. All 11 "severely" affected patients had signs and symptoms of pulmonary edema with cyanosis, persistent cough with frothy sputum, and intense dyspnea. Seven patients of this group died. Autopsy results of 2 of the 3 deaths in the "moderate" group and 2 of 7 deaths in the "severe" group generally supported the clinical findings. No observations of survivors following their hospital discharge were reported.

Lepine and Soucy [19] presented the results of follow-up pulmonary function tests in a worker who had incurred an acute ammonia gas overexposure of undefined concentration or duration. Over a follow-up period of more than one year, the maximum breathing capacity decreased from 97 to 52 liter/minute, the vital capacity from 3.09 to 2.04 liters, and the ratio of residual volume to total lung capacity increased from 49 to 58%. The diffusion capacity as measured by the carbon monoxide method diminished from 9.4 to 6 ml/min. These results indicate moderately progressive airway obstruction and diminishing diffusion capacity.

In 1964 Levy et al [20] reported 4 cases of acute ammonia burns from sudden decompression of ammonia containers. All 4 workers had severe ammonia burns of the face and acute laryngeal edema which was life-threatening and required tracheostomy. The importance of early eye irrigation was also demonstrated in these cases. The only patient who had serious permanent injury to his eyes, resulting in blindness, was the one who did not have early and prompt irrigation. In only one case was there any evidence of residual respiratory symptoms--a persistent, slightly productive cough after 2 years.

In the first case, [20] a 17-year old farm worker was sprayed in the face by a jet of anhydrous ammonia. He had second degree caustic burns of the skin with marked edema of the eyelids. Laryngeal edema developed rapidly, and he quickly became hoarse and dyspneic. He coughed up blood-tinged sputum and expiratory wheezes were heard throughout both lungs. Chest X-rays and routine laboratory tests were normal. He recovered from his pulmonary distress within 15 days, and no permanent impairment of pulmonary function occurred. However, the patient's eye injury resulted in an almost complete loss of vision. Similar farm accidents involved another 17-year old boy and a 61-year old man. Two years later the 17-year old boy still had a productive cough with mucoid sputum, but in spite of corneal scarring, his vision remained normal. The older man showed no impairment of pulmonary function or vision but suffered some atrophic rhinitis, which subsequently improved. In the fourth case, a 28-year old man was struck by a jet of liquid ammonia from refrigeration equipment. He had a postinjury course similar to the other cases, except that he developed pneumonitis in the base of the right lung. There was no residual damage to the lungs or eyes. Pulmonary function tests, 3 years later, were normal in this fourth case.

Mulder and Van der Zalm in 1967 [21] described an acute case which occurred when a tank of ammonium hydroxide overflowed and exposed a worker to a very high concentration of ammonia. Based on the ammonium hydroxide concentration and weather conditions, the ammonia concentration was estimated as 10,000 ppm. The patient immediately experienced cough and vomiting and had difficulty in breathing. The length of exposure was not stated, but he performed "small jobs" for the remaining 3 hours of work before he was seen at a clinic. At that time, his face was red and swollen, he had conjunctivitis, and his mouth and throat were red and raw. His voice was disappearing and he had labored breathing. The heart appeared to be normal, but while X-rays were being taken the heart stopped. He was revived by massage and artificial respiration and was transferred to a hospital. Six hours after the accident his heart stopped again and he died. Autopsy showed marked inflammation of the respiratory tract. Surprisingly, no pulmonary edema was present, but the tracheal epithelium was almost completely denuded.

In 1968 Dupuy et al [22] observed a case of severe gastritis after an unknown concentration of ammonia was inhaled. A truck driver was exposed to ammonia gas from a ruptured container and immediately exhibited evidence of dyspnea and lacrimation. The respiratory symptoms cleared up within 1 day, but for reasons which are not apparent he developed severe, acute gastritis which was confirmed by radiography and gastroscopy. The gastritis improved over the next several months but reappeared later. This apparently is the only published report of damage to the gastrointestinal tract attributed to ammonia exposure.

Osmond and Tallents [23] described a case in which aqueous ammonia was thrown in the face of a teller during a bank robbery. The bank employee developed a marked swelling of the nasopharynx and glottis with difficulties in breathing and swallowing. The authors pointed out that edema of the glottis took several hours to develop and that this delay could give a false impression of less severe damage, thus delaying adequate treatment. A mild chemical pneumonia was produced, from which the man recovered within one week. The chemical burn of his lesser affected eye healed promptly, but the other eye showed gradual deterioration over a 3-week period leading to corneal edema and then opacities, uveitis, and marked impairment of visual acuity. The authors emphasized that first aid must be administered at once, and stated that the only effective first aid for eye exposures of this type "is instant copious irrigation of the injured eye with running water...."

In 1971 White [24] reported that a 20-year old worker was found unconscious in a compression room approximately 5 minutes after he had been overcome by ammonia released from a defective safety valve. No estimates of air concentrations were attempted. He had not been wearing his safety mask and had chemical burns on several parts of the body. Rales were heard in both lungs suggesting fluid in the lower respiratory tract. Five hours later the patient was still unresponsive, and respiration was irregular. There was marked conjunctivitis, and pupils were constricted. Lungs revealed generalized rales and rhonchi with expiratory wheezing, which improved over the next 2 weeks. Six months later the patient had no pulmonary symptoms except a mild bronchitis.

Helmers et al [25] in 1971 presented 4 instances of ammonia injuries in agriculture. In all 4 instances farm workers were sprayed with anhydrous ammonia or ammonium hydroxide. The first worker was sprayed with anhydrous ammonia on the face and chest. Besides showing upper respiratory irritation, he developed pulmonary edema and pneumonitis necessitating a tracheotomy. He recovered within 11 days without any residual lung damage. The second worker was squirted on the skin with several gallons of aqua ammonia. He suffered second-degree skin burns on the exposed areas due to his failure to remove contaminated clothing. The third worker was sprayed in the face with anhydrous ammonia and received facial burns and moderate eye irritation with superficial corneal ulcerations. All 3 of these workers had water available and were able to immediately irrigate the eyes and skin. The fourth worker sustained a severe eye injury from an aqua ammonia spray. He was unable to irrigate his eyes with water until 30 minutes after the accident. Sensation in the more seriously affected eye was lost. Vision was markedly diminished without improvement over the next few months. In spite of cataract surgery four months after the injury, he was left with only light perception. A year later the cornea was considerably vascularized and opacified.

Kass et al [26] in 1972 described 2 cases of bronchiectasis following an unspecified level of exposure to ammonia vapor for a duration of 30-90 minutes. Both cases showed signs and symptoms of severe, acute over-exposure to ammonia following derailment of a railroad tank car containing anhydrous ammonia. They recovered from the acute effects but continued to complain of chronic dyspnea and had a productive cough 2 years after the accident. In the more severe case, the patient was exposed for approximately 90 minutes. Radiologic examination revealed generalized bronchiectatic changes in practically all the segments of the lungs, and pulmonary function tests showed a marked airway obstruction. Hypoxemia was attributed to an uneven distribution between ventilation and perfusion. There was also a marked deterioration of vision with bilateral corneal opacities and early cataract changes. In the less severe case there was radiologic evidence of bronchiectasis involving the left lower lobe and some mild changes in the medial basal segment of the right lower lobe. The results of the pulmonary function tests were interpreted as indicative of obstruction of small airways. In both cases the bronchiectatic changes and the abnormal pulmonary function tests were attributed to ammonia exposure since prior to the accident there was no history of chronic respiratory symptoms, the smoking history was negative, and immunologic disease or genetic defects were not found. The authors emphasized the need for complete pulmonary physiology studies when patients exhibit persistent cough and dyspnea following ammonia exposure.

In 1972 Walton [27] reported 4 ammonia incidents involving 7 men. The autopsy of the one fatal case showed marked laryngeal edema, acute congestion and edema of the lung, and a loss of bronchial epithelium. The remaining 6 were examined at yearly intervals for 5 years. All 6 were classed as "moderate" smokers (15-20 cigarettes a day). Exposures were not described in any detail by the author, however, one man with "light" ammonia exposure exhibited only mild symptoms of bronchospasm and recovered quickly. Forced vital capacity (FVC) and forced expiratory volume in 1 second (FEV 1) were better than predicted values based on sex, age, and height. However, the gas transfer factor (GTF), a measure of diffusion capacity, was low (about 20 ml/min/mm Hg) throughout the follow-up period. This finding was explained by the author as probably associated with the patient's cigarette smoking.

Five men with "heavy" exposure showed acute symptoms and signs of chemical burns of the nose, mouth, and throat; moderate eye irritation; marked dyspnea with cyanosis, cough with blood stained sputum, and pulmonary congestion. [27] There was little evidence of any radiological abnormalities in the chest. Almost all abnormal pulmonary function tests showed a gradual improvement during the first 2 years after the accident. In one case FVC, FEV 1, and GTF were all above predicted values during the entire 5-year follow-up period. In another, the FVC and FEV 1 remained considerably below normal values throughout the follow-up period, while the GTF recovered to nearly normal. Clinical improvement in this second case was noted during the first 2 years but remained unchanged thereafter. In the third case the FVC returned to normal, although the FEV 1 and the GTF remained well below normal. The fourth case showed progressive improvement in ventilation, but a consistent depression of the transfer factor. The fifth case showed gradual improvement to normal for the 2 ventilatory measurements, however the GTF stayed at low normal values. The author [27] attributed the residual abnormal pulmonary function tests in 2 cases (the second and third cases) to the ammonia exposure, whereas in 2 other cases (the fourth and fifth cases) the pulmonary function abnormalities were attributed to their continued smoking habit.

Several additional case histories highlight special problems from ammonia exposure. In 1969 Highman [28] described 2 cases of ocular injuries with a rise in intraocular pressure and cataract formation after ammonia of unknown concentration had been squirted into the victims' eyes during robberies. In both cases, the more severely affected eyes showed marked injection and edema of the conjunctiva; diffuse corneal damage; semidilated, oval, and fixed pupils; and a marked increase of the intraocular pressure which persisted and was controlled only with drugs. Glaucoma was observed to be associated with an open angle. Cataract formation was seen in both cases. Visual acuity was reduced to little more than light perception. McGuinness [29] reported a similar exposure during a jewelry robbery with similar effects, except that the victim did not show an increased intraocular pressure.

Morris [30] encountered 2 cases of possible sensitization to ammonia. The first man developed urticaria on 3 occasions when exposed to ammonia gas coming off an ammonium hydroxide solution at his workplace but the condition cleared up when he stayed away from work. The second worker reported breaking out with the hives once after work and twice when he was riding in a car with workers who had been exposed to ammonia. This apparently is the only report of such an effect, and caution should be exercised before making a causal association.

Shimkin et al [31] observed the development of an epidermoid carcinoma of the nasal septum, which had been burned by an ammonia and oil mixture. They postulated that the corrosive action of ammonia may have prepared, promoted, or exteriorized a latent neoplastic condition. Shimkin et al strongly emphasized that this single case report could not be used to prove causal connections and that additional cases would be required for a critical analysis.

These 15 reports [17-31] involving 81 persons acutely injured by ammonia do not constitute all case reports in the world literature, but do represent a selection displaying the breadth of documented clinical findings from ammonia overexposures, especially those with detailed medical evaluations. In only one instance did the report include an estimate of the air concentration and the duration of exposure for the injured person. Mulder and Van der Zalm [21] reported that a worker died 6 hours following an exposure estimated to be 10,000 ppm for an unspecified time. Of the 81 exposures reported, 16 died, [17,18,21,27] 9 had some evidence of chronic lung disease, [17,19,20,24,26,27] 7 had some evidence of residual visual impairment or a permanent eye lesion, [20,23,25,28,29] 1 had a chronic skin lesion, [31] and 1 had a significant burn scar. [17] All of those with residual lung dysfunction or chronic respiratory symptoms had had documented acute lower respiratory involvement, such as acute tracheitis, bronchitis, bronchopneumonia, or pulmonary edema. Acute symptoms of upper respiratory inflammation, such as acute laryngitis, pharyngitis, or rhinitis, and complaints of acute eye inflammation were reported by all affected persons almost immediately after exposure. Skin burns were reported after direct contact with anhydrous ammonia, [20,24,25,27] aqua ammonia, [25,27,28] and after exposure to concentrated ammonia gas. [26]

C. Human Exposure Experiments

Schmidt and Vallencourt [32] in 1948 exposed one human subject for 4 hours to an ammonia concentration of 530-560 ppm in order to study biochemical and blood pressure changes. Blood urea nitrogen (BUN) and serum creatinine remained unchanged through the exposure. The carbon dioxide combining power of the blood plasma remained unaltered. Repeated blood pressure readings during the experiment showed a linear drop from 127 mm to 102 mm. The authors made no reference to postexposure blood pressures, and data were not given on any subjective reactions or pulmonary function during or after exposure. During the exposure period, the serum nonprotein nitrogen (NPN) gradually increased from 27 mg/100 g blood to 57 mg/100 g blood and the blood ammonia rose from nondetectable levels to values of 36.4 mg/100 g blood. In response to this finding, Ting [33] noted that rats injected with ammonium citrate died at an ammonia nitrogen level of 8-11 mg N/100 ml of blood. Furthermore, assuming a blood volume of 5 liters, a minute volume of 20 liters, and 100% absorption of inhaled ammonia, Silverman and Whittenberger [34] showed that the blood ammonia levels reported by Schmidt and Vallencourt [32] exceeded what was theoretically possible.

Silverman et al [35] in 1949 reported the physiological studies of 7 human subjects exposed to concentrations of 500 ppm ammonia administered for 30 minutes using an oral-nasal mask. All 7 volunteers experienced upper respiratory irritation, lasting up to 24 hours in 2. The subjective reactions of upper respiratory irritation in these 2 were graded as severe; and 2 subjects had marked lacrymation in spite of the exposure being by oral-nasal masks, so there was no direct contact of the eyes. No coughing was noted, however, and the average respiratory minute volume was markedly increased above control values. The respiratory rate was slightly increased. Every 4-7 minutes during the exposure, the minute volume shifted down briefly, but was still well above baseline values. The mechanism of this altered respiration was not elucidated in this investigation. After exposure, respiratory minute volumes fell to levels below the preexposure rate, but returned to preexposure values within 5 minutes after exposure. Silverman et al [35] observed that with 500 ppm delivered for 30 minutes by a naso-oral mask ammonia retention decreased progressively until an equilibrium of 24% retention (ranging from 4-30%) was reached at about the 19th minute (from 10-27 minutes). Ammonia in the expired breath was not detectable beyond the 8th minute after exposure. Contrary to the results reported by Schmidt and Vallencourt, [32] the indices of nitrogen metabolism--BUN, NPN, urine urea, and urine ammonia--all remained normal. The carbon dioxide combining power remained unchanged. Pulse rate and blood pressure were measured in 2 of the 7 subjects. In one of these there was a 15% increase in pulse rate and a 10% increase in blood pressure. These changes promptly returned to baseline when exposure was discontinued, and there was no change in the second individual. The limitation of symptoms to the nose and throat suggested to the authors that ammonia was absorbed largely by the upper respiratory tract.

In 1950, Landahl and Herrmann [36] reported an investigation of the short-term retention of ammonia in the nose of 4 human subjects. A face mask with 2 tubes attached was used. One tube supplied the gas-air mixture, the other was used for air sampling. In this nasal retention experiment, the subject held his breath while a gas-air mixture was drawn in through the nose and out through the mouth. A parallel air stream from the same source was sampled simultaneously to determine the initial ammonia concentration. When a concentration of 0.05 mg/liter (approximately 72 ppm) was drawn through the nose at a rate of 18 liters/minute, an average of 83±5% was retained. A threefold increase of the rate of intranasal flow resulted in a moderate decrease of the percentage retained. When the ammonia gas was inhaled and exhaled through the mouth, bypassing the nasal passage, the total retention was about 92%. In this experiment the subject inhaled through the mouth by a gas-air mixture tube and exhaled into a sampling tube. The percentage retained was not significantly affected by increasing the concentration from 0.04 to 0.35 mg ammonia/liter (approximately 58 ppm to 503 ppm). A threefold increase of the time the ammonia remained in the respiratory tract resulted only in a negligible increase of the percentage retained. No data were given of any subjective reactions or pulmonary function changes during or after exposure.

For comparison with human responses to monomethylhydrazine, MacEwen et al [37] exposed 6 volunteers at ammonia concentrations of 30 and 50 ppm for 10 minutes. Subjects did not know the concentrations to which they were being exposed and exposures were made in random order.

Concentrations, which were continuously monitored, were established and stabilized in a Rochester Chamber. Test subjects then inserted their heads through a rubber diaphragm for the 10 minutes of exposure. The irritation was rated subjectively on a scale of 0-4 and odor on a scale of 0-5. Results for the 2 ammonia concentrations are given in Table XI-3. At 50 ppm, irritation was rated as "moderate" by 4 of the volunteers, but 1 individual reported no detectable irritation. None of the subjects found the irritation at 50 ppm to be "discomforting" or "painful." All of the subjects rated odor as "highly penetrating" at 50 ppm, and 3 volunteers gave the same rating at 30 ppm.

The Industrial Bio-Test Laboratories Inc [38] has also evaluated the irritation threshold of ammonia. Ten human subjects were exposed at 4 different concentrations (32, 50, 72, and 134 ppm) for 5 minutes. The criteria of irritation were any annoyance to the eyes, nose, mouth, throat, or chest which persisted throughout the 5-minute exposure period. The investigators felt that an exposure of 5 minutes was adequate "since irritation with such a material depends more upon concentration than upon time of exposure." The frequency of positive findings out of the 10 subjects exposed to each concentration were as follows: at 32 ppm 1 subject complained of dryness of the nose. At 50 ppm 2 subjects had dryness of the nose. At 72 ppm 3 subjects experienced eye irritation, 2 had nasal irritation, and 3 had throat irritation. At 134 ppm 5 subjects showed signs of lacrimation, 5 had eye irritation, 7 had nasal irritation, 8 had throat irritation, and 1 complained of chest irritation. Because the only reaction noted at 32 and 50 ppm was slight dryness of the nose, the authors concluded that "concentrations of 50 ppm or less did not cause irritation or discomfort." However, this study involved only a 5-minute exposure, and it is possible that on much longer exposure irritation might have developed; it is also possible that on longer exposure acclimatization could have developed.

Patty [39] stated that he observed that a 1% concentration of ammonia was mildly irritant to the moist skin, at 2% the irritation was more pronounced, and that a concentration of 3% or greater caused a stinging sensation and "may produce chemical burns with blistering after a few minutes exposure." The specifics of this experiment apparently have never been published.

In summary, the above 6 human inhalation studies [13,32,35-38] and the 1 report [39] on skin exposure were directed toward identifying acute responses to ammonia with exposure times of several hours or less. Unfortunately, these studies do not indicate at what air concentrations short-term exposures may result in ventilatory abnormalities, such as significant decrements in FEV 1. In addition, subjective responses of upper respiratory and eye irritation have not been developed into a reliable graded response measurement so as to compare results of various inhalation concentrations and durations of exposure. Thus, only crude indicators of physiologic response were available. Furthermore, the question of skin response to varying concentrations of ammonia appears to be very poorly documented.

Epidemiologic Studies

El Sewefy and Awad [40] evaluated 41 persons employed by an ice manufacturing plant in Egypt. Air concentrations of ammonia were not given, but the authors reported that the workers were exposed to a temperature of -6 C in the ice plant. Workers moved in and out of the refrigerated area, thereby being subject to temperature differences of up to 44 C in the summer. At the time of the study, the workers had an average 16.1 years of exposure and were somewhat older than the 28 control employees, who came from "non-hazardous" work places. For analysis of the data, the subjects were divided into smoker and nonsmoker groups. The exposed workers in both the smoker and nonsmoker groups were slightly older and shorter than the corresponding groups of control workers. Pulmonary function tests (FVC and FEV 1) for smokers vs nonsmokers were compared in both groups and were not significantly different. Therefore, smoker and nonsmoker data were combined to compare control and exposed workers. Values were lower in the exposed group, but the difference was not statistically significant at the 5% level when corrected for age and height differences. Chest symptoms (cough, phlegm, wheeze, and dyspnea) in the ammonia exposed group and control group were not significantly different. The authors concluded that the combination of long-term exposure to ammonia and extreme temperature changes in this plant did not have any adverse effect on ventilatory function or respiratory symptomatology.

Bittersohl [41] reported that in the German chemical industry cancer morbidity and mortality among male and female workers for the period from 1958-1967 was very high, especially in the ammonia and amine plants. The average air concentration in these 2 plants was estimated to be 2-3 times the German Democratic Republic (East Germany) maximum allowable concentration (MAK) of 25 mg/cu m (approximately 35 ppm). The duration of employment was more than 10 years for about 80% of the work force. The 10-year cancer morbidity rate for the entire chemical factory of about 30,000 workers was approximately 160/10,000/year. In 1 of the 2 ammonia plants, the morbidity rate per 10,000 employees was reported to be about 1,250 in males and about 370 in females. The male cancer morbidity rate was about 1,000 for the second plant (precise rates were not given, but must be read from bar diagrams). The author suggested that the average ammonia exposure dose had been greater for male workers in the ammonia plants. Cancer deaths reportedly accounted for 40% of all deaths among employees of the ammonia plants during this 10-year period. Bittersohl also noted that his analysis of the distribution of cancer deaths by site suggested an excess of lung, urinary tract, gastric, and lymphatic neoplasms.

Details in this paper are very poor. The author did not include the background information necessary to judge the accuracy of his conclusions. This isolated and poorly documented report is not adequate to implicate ammonia as a suspected carcinogen, but it does make more urgent the need for follow-up epidemiological studies. Until thorough studies are completed, the validity of this single report cannot be evaluated.

Elkins [42] stated briefly without giving any details that ammonia concentrations of 125 ppm in a mildew-proofing process were definitely irritating, while 55 ppm in an electroplating plant "were judged not to be excessive."

In 1955 Vigliani and Zurlo [43] reported on their investigations of exposures to 24 substances. They reported that in an "ammonia works" concentrations of 100 ppm could not be continuously inhaled for lengthy periods without irritation of the upper respiratory tract and eyes. They also reported that workers accustomed to 20 ppm of ammonia did not complain but showed slight redness of the conjunctiva. Those not accustomed did have eye and respiratory discomfort and irritation. The authors recommended a MAC of 50 ppm. It is not clear whether respiratory complaints pertained to the upper or lower respiratory tract or whether conjunctivitis was more severe in the nonaccustomed workers. Unfortunately, the details of these surveys were not provided, namely, the numbers of workers at risk at 100 and 20 ppm, the numbers and matching of controls, the environmental measurement data, the methods of measurement of clinical effects and subjective responses, the proportions and persistence of those showing effects, or the presence of confounding variables such as other irritants or preexisting chronic diseases.

Mangold [44] in an unpublished report evaluated complaints of eye irritation in a blueprint shop. Two 2-hour samples on each of 2 days and 10 15-minute samples of air on each of 2 later days during a 1-week period when eye complaints were occurring showed concentrations of ammonia ranging from 4-29 ppm. No reference was made to the type or level of any respiratory complaints, if any, of the workers in the blueprint shop. Previous evaluation 6 months earlier in the same shop had reported air levels below 5 ppm of ammonia associated by the workers and/or the hygienist with barely noticeable eye irritation. It was concluded that intermittent peak exposures in the range of 20 ppm of ammonia caused moderate eye irritation. The author considered these to be strictly irritating or annoying but not injurious exposures. This was a very small survey (8 workers) in which the effects were entirely subjective and were given only in descriptive, not quantitative, terms. There are no data on how many of the 8 workers were affected, the possible presence of other irritants such as coupling agents or cigarette smoke was not acknowledged, the association of peaks with acute responses was not documented, and there was no clinical verification of any of the responses.

Pagnotto [written communication, September 1973] reviewed the files of surveys performed by the Division of Occupational Hygiene of the Commonwealth of Massachusetts from 1940 to 1972. Several plant surveys mentioned irritating effects. A survey of refrigeration equipment in an ice cream plant disclosed that ammonia concentrations in air ranged from 9-37 ppm. Odor fatigue was reported at these concentrations by the industrial hygienist, who stated that the odor of ammonia was noticeable but that "the sense of smell was quickly deadened to the presence of the gas." In an insole cementing operation, ammonia concentrations were 15-28 ppm in the work area, and very slight eye irritation was reported. A concentration of 45 ppm was found in a blueprint machine room, and the industrial hygienist commented that there was "some eye irritation, but one quickly becomes accustomed to it." Samples ranging from 3-29 ppm were collected near a printing machine with the comment from the industrial hygienist that the "odor of ammonia was quite marked, but not disagreeable." In another survey at a printing machine, the range was 2-45 ppm, but the hygienist commented only that the "odor of ammonia was strong" when taking the sample of 45 ppm. None of these brief reports were epidemiologic studies in which the investigator used systematic methods for evaluating the effects, used control groups, noted the frequency of clinically substantiated or reliable subjective responses among workers at risk and controls, documented carefully the environmental exposures of all those at risk including confounding exposures, or attempted statistical comparisons of the incidence of the various acute effects.

In the preceeding 4 reports, [42-44, and LD Pagnotto, written communication, September 1973] irritation was associated with a wide range of ammonia exposure. The highest concentration reported, 125 ppm, [42] was "definitely irritating," while "barely noticeable" eye irritation was reported [44] at 5 ppm. However, in one survey mentioned by Pagnotto, [written communication, September 1973] the hygienist who collected a sample of 45 ppm noted the strong odor of ammonia but mentioned no irritation. Elkins [42] considered exposure at 55 ppm not to be "excessive," and Vigliani and Zurlo [43] recommended 50 ppm as a MAK.

Animal Toxicity

A. High Exposure Studies

In 1933, the Underwriters Laboratory [45] reported exposures of 8 guinea pigs to concentrations of 0.5-0.6% by volume (5,000-6,000 ppm). Two animals were removed from the test chamber at the end of 5, 30, 60, and 120 minutes and all were observed for 10 days. Within 30 seconds, all 8 were lachrymating profusely, discharging from their noses, and exhibiting labored breathing. At the end of 5 minutes, their eyes and noses were intensely inflamed, respiration was irregular, and frequent retching movements were noted. Violent coughing occurred after 30 minutes, breathing was shallow at 60 minutes, and barely perceptible at 120 minutes. All animals survived but showed increasing severity of respiratory irritation depending on exposure time. All 8 animals were blind, as judged by corneal opacities, when first removed from the chamber, but those exposed only 5 minutes recovered their sight within a week. Sight was recovered by 1 animal exposed for 30 minutes and in only 1 eye of 1 animal exposed for 60 minutes. Aside from this permanent blindness in 5, all animals recovered and showed consistent weight gain during the 10-day observation period.

A second group of 4 guinea pigs was exposed [45] to concentrations of 2.0-2.5% by volume (20,000-25,000 ppm). Two animals removed after 5 minutes were blind and showed signs of marked respiratory irritation. Except for permanent blindness in 1 of the 2 guinea pigs, both recovered fully within one week. One animal died after 9 minutes of exposure, apparently as a result of a reflex stoppage of the respiration since autopsy findings were minimal. The fourth animal, exposed for 30 minutes, displayed marked respiratory difficulties, but recovered except for permanent blindness.

Silver and McGrath [46] in 1948 exposed 9 groups of 20 mice to ammonia for 10 minutes, each group at a different concentration. Exposures ranged from 6.1-9.0 mg/liter (approximately 8,770-12,940 ppm). The LC50 was estimated to be 7.06±0.32 mg/liter (about 10,150 ppm). All test animals exhibited great excitement and severe eye and upper respiratory tract irritation. They closed their eyes immediately and within one minute they were gasping, pawing, and scratching their noses. Death with convulsions occurred after about 5 minutes, and 100 of 180 animals died before the 10-minute exposure was completed. The 80 surviving animals recovered rapidly after removal from the chamber, showing normal behavior in many cases within 10 minutes. Between the 6th and 10th postexposure days, 7 of the 80 died, compared with no deaths in controls. Autopsies were not performed.

Boyd et al [47] in 1944 reported an experiment in which they exposed an unstated number of rabbits and cats for 1 hour to initial concentrations of 3.5-8.7 mg/liter (approximately 5,200-12,800 ppm) with an average concentration of 7.0 mg/liter (approximately 10,360 ppm). This was reported to be the "approximate LC50." The authors estimated that the static method of gassing used probably resulted in an average concentration of half the initial concentrations or less. Boyd and associates also evaluated the gas absorption of the nasobuccopharyngeal section of the respiratory tract. One group of rabbits inhaled directly through a tracheal cannula, and a second group inhaled normally through nose, mouth, and throat. The numbers of rabbits in the 2 groups were not indicated by the authors. The mean survival time in the second group was reported to be almost twice that of the first group, 33 hours versus 18 hours. On microscopic examination, the trachea was congested and edematous. The mucosa was necrotic and sloughed off in 80-90% of the animals in which the upper respiratory tract had been bypassed, while the trachea was normal in appearance in the second group of test animals. Similar differential findings, but to a lesser degree, were shown in the bronchial mucosa. The damage to the bronchioles and alveoli surprisingly appeared to be identical in both groups. It was described as congestion, edema, hemorrhage, and atelectasis with emphysema. The authors concluded that the upper respiratory tract acted as a protection only to the trachea and bronchi, and that small airways and alveoli were less resistant to ammonia injury than the upper airways. The data are difficult to interpret because of lack of information on the number of animals used and the number affected.

B. Low and Moderate Exposure Studies

Weedon et al [48] in 1940 reported on continuous flow chamber studies in which they exposed 8 rats and 4 mice for 16 hours to an ammonia gas concentration of 1,000 ppm. They reported no noticeable effects during exposure. One rat died 12 hours after exposure and showed congestion of the brain, liver, and kidneys, plus large hemorrhages in the lungs and pulmonary edema. The other 11 animals showed no gross abnormalities during the subsequent 5 months of observation. Two rats and 2 mice were killed at that time, and autopsy results were negative.

Weatherby [49] in 1952 reported an experiment in which he exposed 12 guinea pigs to about 170 ppm ammonia for 6 hours a day, 5 days a week for up to 18 weeks. Chamber concentrations were monitored and ranged from 140-200 ppm. The 12 exposed animals and 6 controls were weighed weekly. No adverse effects were observed by autopsy of the 4 exposed and 2 control animals killed after 6 weeks or after 12 weeks. In 4 animals exposed for 18 weeks, there was congestion of spleens, livers, and kidneys with early degenerative changes in suprarenal glands. Increased blood destruction was suggested by higher quantities of hemosiderin in the spleens. In the upper tubules of the kidneys there was cloudy swelling with precipitated albumin in the lumen and some casts. These changes were also seen in the lower tubules of 2 animals. The cells of the suprarenal glands were swollen and the cytoplasm in some areas had lost its normal granular structure. The author considered all changes to be relatively mild, though definite.

Coon et al [50] in 1970 reported experiments in which they exposed 15 rats, 15 guinea pigs, 3 rabbits, 2 dogs, and 3 monkeys to an ammonia concentration of 155 mg/cu m (about 220 ppm) for 8 hours a day, 5 days a week for 6 weeks. This concentration did not produce any abnormal pathologic findings in any of the species except evidence of focal pneumonitis in the lung of 1 of the monkeys. Exposure of the same numbers and species of animals to 770 mg/cu m (approximately 1,110 ppm) for the same duration produced mild to moderate eye irritation and labored breathing in the rabbits and dogs at the beginning of exposure, but these disappeared by the second week and no other signs of irritation or toxicity were noted. Necropsy revealed nonspecific inflammatory changes in the lungs of the rats and guinea pigs at the end of the exposure period.

In addition to these studies, several experiments were undertaken by Coon et al [50] involving continuous (24 hours a day, 7 days a week) exposure to ammonia. Continuous exposure to 40 mg/cu m (about 60 ppm) for 114 days showed no sign of toxicity in any of the species referred to above. Macro- and microscopic examination showed no lung abnormalities. Forty-eight rats continuously exposed to 127 mg/cu m (about 180 ppm) for 90 days did not reveal any abnormalities of organs or tissue. Inhalation of 262 mg/cu m (approximately 380 ppm) for 90 days produced mild nasal irritation in about 25% of 49 rats and a slightly elevated leucocyte count in 4 of the rats. Fifty of 51 rats continuously exposed to 455 mg/cu m (about 650 ppm) died by the 65th day of exposure. Mild nasal discharge and labored breathing were exhibited by all animals, but no microscopic examinations were made on these animals. In a final experiment, all species mentioned above were continuously exposed to 470 mg/cu m (approximately 680 ppm) for 90 days. Four of 15 guinea pigs died and 13 of 15 rats died. Marked eye irritation was noted in dogs and rabbits, with corneal opacities in about one-third of the rabbits. At necropsy all test animals examined had more extensive focal or diffuse interstitial inflammatory processes in the lungs than did controls.

Stombaugh et al [51] in 1969 evaluated the effects of ammonia on pigs. One pig exposed to 280 ppm showed immediate irritation of the nose and mouth and abnormal respiratory patterns, and by the 36th hour of exposure had convulsions and extremely shallow and irregular breathing. Convulsions continued for 3 hours after exposure ended but the animal appeared normal several hours later. In each of 2 trials, 4 exposure groups of 9 pigs each were continuously exposed to ammonia for 5 weeks. Data from both trials were combined for analysis. Concentrations of ammonia were measured daily, and the average exposures of the groups were 12, 61, 103, and 145 ppm. Feed consumption and average daily weight gain were adversely affected by increasing ammonia concentrations. Pigs exposed to the 3 higher concentrations had excessive nasal, lacrymal, and oral secretions, but these were less pronounced in those exposed to 61 ppm. Pigs exposed to 61 ppm appeared to adjust within 3-4 days, so that their secretory rate was only slightly higher than that of animals exposed to 12 ppm. Pigs in the 2 higher concentrations coughed approximately 3 times as much as those in the lower, and coughing at 61 ppm was slightly more frequent than at 12 ppm. Five animals from each exposure group were autopsied and all gross and microscopic findings were normal.

Doig and Willoughby [52] found no adverse effects on food intake, weight gain, or frequency of coughing when weanling pigs were continuously exposed to ammonia for up to 6 weeks at an average concentration of 106 ppm, with a range from 52-160 ppm. Slight eye irritation with evidence of photophobia and excessive lacrimation were noticed during the first week of exposure, but thereafter the pigs appeared to be acclimatized. The hematocrit, total white blood cell count, differential white cell count, and serum lactic dehydrogenase activity were unchanged. Bacterial flora in the trachea of exposed pigs did not differ from that of control animals, but pathologic changes were noted in the tracheal epithelium with an increase in epithelial thickness and a decrease in the number of goblet cells. Effects on bronchi, bronchioles, and alveoli were not observed. One pig was randomly selected each week for autopsy studies that included estimating the thickness of the tracheal epithelium. The 6-week mean for exposed pigs was 32.9 μm vs 19.4 μm in controls. Likewise, the mean number of goblet cells per 500 μm was 10.6 for exposed animals and 18.9 for controls. These changes were not evident in the animal autopsied after 1 week, but they were seen in all 5 animals examined in succeeding weeks.

Corn starch dust and corn dust were studied [52] for interaction with ammonia by replicating the ammonia exposure with simultaneous exposure either to corn starch dust or to corn dust. The authors concluded that the dust inhibited the effects of ammonia on the trachea. The average corn starch dust concentration was approximately 70 mg/cu m with a median particle size of about 3 μm, and the corn dust concentration was approximately 3 mg/cu m with a median particle size of about 1 μm. Limited data were presented to indicate that the epithelium of the nasal turbinates also underwent changes suggestive of chronic inflammation.

Mayan and Merilan [53] in 1972 used thermocouples in plastic masks secured over test animals' noses and thereby recorded respiration on magnetic tape. In 5 animals BUN, blood pH, and blood carbon dioxide were measured prior to exposure and immediately following exposure to 100 ppm of ammonia. Using 2.5-3.0 hour exposure times, 9 rabbits were exposed to 50 ppm in a total of 22 trials, and 7 rabbits were exposed to 100 ppm in 16 trials. Five animals of the latter group were included in the biochemical studies. A significant decrease of about 33% in the respiration rate of rabbits exposed to both concentrations was reported. Respiratory depth was measured indirectly by the thermocouple sensors, and the authors reported that respiratory depth increased with time during exposure to ammonia. In 5 rabbits exposed to 100 ppm ammonia, BUN disclosed significant increases from 19.4 to 24.6 mg/100 ml (P less than 0.005) and blood carbon dioxide rose from 14.3 to 18.9 meq/liter plasma (P less than 0.07). The blood pH was not significantly altered. No pathological changes in lungs, liver, spleen, or kidneys were found.

C. Ciliary Function and Related Studies

Cralley [54] noted a cessation of ciliary activity without recovery in resected sections of rabbit trachea exposed in a tissue chamber to 500 ppm ammonia for 5 minutes and 400 ppm for 10 minutes. Temporary cessation was observed at 200 ppm after 9.5 minutes of exposure of the trachea.

Dalhamn [55] in 1956 studied rats whose incised tracheas were exposed directly to ammonia without passage through the upper respiratory tract and microscopically observed ciliary activity in vivo. Control preparations using moist, warm air showed no effect on ciliary movement or mucosal drying with a 10-minute treatment. Ciliary activity of the trachea ceased after exposure for 5 seconds at 90 ppm, after 10 seconds at 45 ppm, after 20 seconds at 20 ppm, after 150 seconds at 6.5 ppm, and after 7-8 minutes at 3 ppm. Recovery occurred in all cases 10-30 seconds after exposure was discontinued. All reported data were based on the average of 3 observations for each exposure. Findings at the 2 lower concentrations were, according to the author, inadequate because the gas sampling method used was applicable only to concentrations of 5 ppm or more. The following studies by the same author did not verify the findings of this earliest experiment.

In 1963, Dalhamn and Sjoholm, [56] using the same in vivo preparation, reported that 500-1,000 ppm caused arrest of ciliary activity in an excised trachea of a rabbit following a 5-minute exposure. Also in 1963, Dalhamn [57] reported that, in resected rabbit tracheas, concentrations of about 1,000 down to 460 ppm stopped ciliary activity, and at 400 down to 270 ppm the ciliary beat either ceased or was greatly reduced. Below 260 ppm an effect could be detected only by counting ciliary beats. In this way, 100 ppm was established as the approximate level at which a reduction first occurred. Dalhamn [57] then exposed excised tracheas to 75-169 ppm. Using cinematographic recordings of microscopic images, the range of initial ciliary beat rates was established as 1,111-1,603 beats/min. Postexposure rates averaged 7.5% lower than initial ciliary beat rates for concentrations between 112 and 169 ppm. No mean difference was observed between 88 and 75 ppm. The author estimated that 100 ppm was the lowest concentration that would produce a significant reduction in ciliary motility using this technique.

In further experiments on 6 rabbits, Dalhamn [57] reported that a concentration of about 2,000 ppm introduced for 45 minutes into the nasal cavity produced concentrations of about 100 ppm in the rabbit trachea. Ten rabbits were then exposed to an average concentration of about 2,200 ppm for 45 minutes. Cinematographic recordings of ciliary activity were obtained after 15, 30, and 45 minutes of exposure. A significant mean decrement of 17% in ciliary activity was noted after 45 minutes. Ten rabbits were also exposed to ammonia at about 2,000 ppm and pulverized carbon particles at an average concentration of about 2.0 mg/cu m and with a median particle size of about 1 μm. After 45 minutes the mean decrement in ciliary activity was 33%. Dalhamn did not consider this interaction to be of practical significance.

Dalhamn and Reid [58] also examined the interaction between ammonia and carbon particles. Four groups of 10 rats each were exposed either to air alone, carbon particles (median diameter slightly under 1.0 μm) at a concentration of 7 mg carbon/cu m, ammonia at a mean concentration of 102 ppm, or to ammonia plus carbon particles at concentrations of 119 ppm and 3.5 mg carbon/cu m, respectively. Exposures lasted 5 hours a day, 5 days a week for 60 days. At the end of that time, ciliary activity was determined and sections of trachea were taken for microscopic examination of the mucosa. Neither ammonia alone nor carbon alone had a significant effect on ciliary activity, but the combination of ammonia and carbon produced a significant reduction in ciliary activity. On microscopic examination, the tracheal mucosa was classified as "normal," "moderately damaged," or "severely damaged." Among the air controls and the rats exposed to carbon alone, none of the tracheas were severely damaged and 2 in each group were considered to be moderately damaged. The remainder, 8 of the air controls and 7 of those exposed to carbon, had normal tracheas (the section from 1 rat exposed to carbon alone was not suitable for microscopic examination). Of those exposed to ammonia alone, 4 rats had normal mucosa, 3 had moderately damaged, and 3 had severely damaged mucosa. In contrast, there were no normal tracheas in rats exposed to ammonia plus carbon particles. Two of these rats showed moderate damage and 8 rats had severe damage.

In summary, animal experiments indicate that the main toxic effect of ammonia is on the respiratory tract and on the eyes. Exposure at concentrations of 5,000-6,000 ppm for up to 2 hours produced marked irritation of the respiratory system and produced blindness in many animals exposed for 30 minutes or more. One of 2 guinea pigs exposed at 20,000-25,000 ppm for 5 minutes was permanently blinded, 1 died after 9 minutes, and 1 which survived for 30 minutes was permanently blinded. [45] The LC50 for the animals exposed for 10 minutes [46] and for 1 hour [47] was reported to be in the range of 10,000 ppm. Simulating a workweek, intermittent exposure to concentrations of about 1,000 ppm for 6 weeks, produced mild to moderate eye inflammation and labored breathing in some animals, and inflammatory lung changes in others. [50] Similar intermittent exposures to concentrations of about 200 ppm were reported to have no adverse effects on the respiratory system of rats, guinea pigs, rabbits, and dogs, but 1 of 3 monkeys showed focal pneumonitis. [50] Intermittent inhalation exposures of rats to about 100 ppm for almost 10 weeks showed chronic inflammation of the trachea and a ciliary motility effect, potentiated by activated carbon particles. [58]

In continuous 24-hour exposures over prolonged periods the effects of ammonia were, as might be expected, more severe. Exposure up to about 180 ppm for several months did not produce adverse effects, but 380 ppm and more produced nasal discharge, labored breathing, and, at 680 ppm, inflammatory processes in the lungs. [50] At concentrations in the range of 100-150 ppm, slight eye and upper respiratory irritation were noted early in the exposure, [51,52] and marked thickening of the tracheal epithelium was found at autopsy. [52]

Correlation of Exposure and Effect

A worker exposed to an ammonia concentration estimated at about 10,000 ppm experienced immediate coughing, dyspnea, and vomiting. [21] The worker died of heart failure 6 hours following the exposure. The autopsy showed denudation of the tracheal epithelium.

During controlled human exposures at about 500 ppm for 30 minutes [35] the following were observed: irregular minute ventilation with a cyclic pattern of hyperpnea, increases in blood pressure and pulse rate, variable lacrimation, and general complaints of upper respiratory irritation, some of these persisting for 24 hours following exposure.

Exposures of human subjects to 134 ppm for 5 minutes produced lacrimation, eye irritation, discomfort of the nose and throat in some individuals, and 1 complaint of discomfort in the chest. [38] In plant surveys with exposures at 100-125 ppm, [42,43] definite upper respiratory and eye irritation have been reported. At 72 ppm for 5 minutes a "discomfort" level of nasal and throat irritation plus eye irritation were reported by some subjects. [38]

MacEwen et al [37] exposed volunteers to ammonia concentrations of 30 and 50 ppm for 10 minutes and reported 4 of 6 subjects felt "moderate" irritation at 50 ppm, while the remaining 2 volunteers felt no irritation and "just perceptible" irritation, respectively. There was no or "just perceptible" irritation at 30 ppm. The odor was considered to be "highly penetrating" at 50 ppm by all subjects and by 3 at 30 ppm, including one who reported irritation to be imperceptible at both 30 and 50 ppm (Table XI-3).

Exposures of 5 minutes at 32 and 50 ppm produced no eye irritation but some complaints of dryness of the nose. The investigators reported the latter effect was not one of discomfort. [38] In a survey of an electroplating plant, the industrial hygienist was aware of "no adverse effects" at an average concentration of 55 ppm. [42]

On the other hand, a number of plant surveys have suggested that lower concentrations do produce an adverse response in some workers. In one plant with average concentrations of 20 ppm, [43] some workers displayed conjunctivitis, and "unaccustomed" workers complained of eye and respiratory irritation. In a blueprint shop [44] several workers noted only "barely noticeable eye irritation" at 5 ppm or less. The industrial hygienist associated eye irritation with peaks of about 20 ppm. [44] "Very slight eye irritation" was reported by workers in an insole cementing operation with exposures ranging from 15-25 ppm, and in another blueprint room with concentrations of 45 ppm there were complaints of eye irritation. [LD Pagnotto, written communication, September 1973]

Animal studies suggest that some airborne particulates can potentiate the effect of ammonia, apparently by carrying adsorbed ammonia deeper into the respiratory tract. Doig and Willoughly [52] found that corn starch dust and corn dust inhibited the effect of ammonia on pig tracheas. In contrast, Dalhamn [57] and Dalhamn and Reid [58] found that activated carbon particles increased the tracheal damage in rats.

IV. ENVIRONMENTAL DATA

Sampling and Analytical Methods

Of the methods evaluated for analysis of ammonia in air, several offer acceptable sensitivity, specificity, precision, and accuracy. The method of choice for sampling and analysis is detailed in Appendices I and II. It entails the scrubbing of air with a midget impinger containing dilute sulfuric acid and color development with Folin-Nessler's Reagent.

Several adaptations of chemiluminescence based upon the oxidation of ammonia to nitric oxide have been reported to have varying degrees of efficiency. [59,60] Lasers have been utilized by Shimizu, [61] Kreuzer et al, [62] and Hinkley and Kelley [63] for spectophotometric determination of ammonia. Greatly increased sensitivity is possible, but the availability, expense, and operator expertise requirements of these instrumental procedures place their practical application out of reach for most industrial hygiene laboratories.

The selective ion electrode apparently will obviate, upon documentation of its specificity, accuracy, and precision, the need for chemical analysis of impinger samples. Sensitivities seem to be adequate. [64,65] The interferences from volatile amines will also have to be taken into consideration.

Some additional analytical techniques include enzymatic assays, [66,67] pyridine-pyrazole, [68,69] indophenol color development, [70-73] gas chromatography, [74,75] ninhydrin color development, [76] coulometry, [77] and conductometric diffusion, [78] These methods have a combination of shortcomings including incompatible sampling requirements and lack of sensitivity and accuracy. They do have the potential for adaptation to workable air monitoring techniques.

The colorimetric determination of ammonia using an alkaline solution of mercuric iodide and potassium iodide was first proposed by Nessler in 1856. [79] The ammonia reacts with Nessler's reagent to form a colored colloid that is subject to flocculation on standing, [68,80,81] but the control of alkalinity and the appropriate potassium iodide excess help to reduce this problem. [68,81] Volatile amines, aldehydes, acetone, alcohols, and ammonium salts interfere with the Nessler method. [68] Formaldehyde has been reported [69] to interfere quite strongly.

Sampling frequency should be adequate to describe the fluctuations of every operation, particularly maximum concentrations of ammonia. Samples can be collected with bubblers [82] or impingers [69] containing 0.02 N sulfuric acid. Okita and Kanamori [69] reported that 7 ppm ammonia was collected in impingers with an efficiency of 94.8-99.5% when sampled for 3-16 minutes at flow rates of 0.5-3.0 liters a minute. In contrast, 0.03 ppm ammonia was collected with an efficiency of only 58% when sampled for 95 minutes at a flowrate of 1.5 liter a minute, and 62% when sampled for 120 minutes. A glass fiber filter impregnated with 5 N sulfuric acid collected 95.3-98.0% of the ammonia in 3 1-hour tests at a flowrate of 15 liters a minute. Because of the potential health hazards associated with the improper use of mercury compounds, the Nessler's reagent must be handled and disposed of with care.

Ammonia detector tubes provide a quick, relatively simple, and reasonably accurate method for spot checking potential exposure areas. If the limits in accuracy are recognized, detector tubes may be useful for determining areas which require compliance with various sections of the recommended standard or which require more detailed industrial hygiene surveys. A number of ammonia detector tubes have been tested and certified by NIOSH [83] in accordance with the provisions of 42 CFR 84, as amended. Basically, in order to be certified detector tubes must exhibit 1) accuracy within ±35% at half of the NIOSH Test Concentration (NTC) and ±25% at 1, 2, and 5 times the NTC (for ammonia, the NTC is 50 ppm); 2) channeling (beveled stained-unstained interface) of less than 20%; and 3) tube reader deviation (standard deviation estimate of 3 or more independent readers) of less than 10% of the average of the readers. Detector tubes are subject to positive errors (high readings) in the presence of amines and negative errors (low readings) in the presence of acid gases. Another device for making "on the spot" evaluations and instructions for its fabrication was reported by Gisclard et al. [84] This device consisted of a 100 cc syringe used to draw air through 0.0001 N sulfuric acid containing methyl purple indicator. Although the device actually indicates only total alkalinity, the ammonia concentration could be estimated based on the air volume necessary to cause a color change.

Environmental Levels and Engineering Controls

Little information has been published concerning workroom levels of ammonia encountered in industry, or the control measures used and their effectiveness. The workroom levels that have been reported are not high, suggesting that adequate control may be readily obtained by use of local exhaust ventilation. In 1971 Carlsson [85] found 5-50 ppm ammonia in chicken houses as a result of decomposing floor litter and bedding material. The lower concentrations were found at the beginning of the growing period for broiler production, and the higher concentrations at the end when the chickens were caught and the chicken houses were cleaned. Ventilation intakes near the ceiling of chicken production buildings did not control the ammonia which was produced near the floor. Recommended remedial measures included complete redesign of chicken production facilities, with interim relocation of ventilation intakes to floor level.

Mangold [44] investigated complaints originating in a reproduction department using diazo-type machines. The ammonia concentration in 2 2-hour samples was 8 ppm with room windows closed and machine ventilation operating. In 2 similar samples taken the next day levels were 10 and 17 ppm. Mangold felt that peak concentrations of ammonia were probably responsible for the complaints since concentrations determined up to that time had been low. Sequential samples were then taken over 2 working days, representative of the breathing zone air for workers receiving treated paper from the machine onto a cutting table. Fifteen-minute samples with 30-minute periods intervening showed a range of 4-29 ppm. Highest concentrations occurred when the machines were stopped for the noon break and ventilation was shut off. Mangold concluded that the existing machine ventilation was effective for control of ammonia emitted by the machinery, but that it did not control the ammonia escaping from the processed paper extruded from the machines onto the cutting table. Other levels measured for a variety of processes are listed in Table XI-4. [42,86,87]

Although over 80% of the ammonia manufactured is used as fertilizer or for fertilizer manufacture, [5] investigations of low level exposures in agricultural operations have not been found. Reports of accidental acute exposures in agricultural operations indicate the serious nature of such occurrences. [25,88] All of the papers surveyed underscored the need for care and safe work practices any time ammonia is used, but this is especially true in agricultural operations.

V. DEVELOPMENT OF STANDARD

Basis for Previous Standard

In 1943 the US Public Health Service [89] published toxic limits for various substances. The maximum allowable concentration (MAC) for ammonia was given as 100 ppm. No basis for this value was given except to state that it was the most widely accepted value.

In 1945, Cook [90] reviewed the MACs of industrial atmospheric contaminants as promulgated by a number of states (California, Connecticut, Massachusetts, New York, Oregon, and Utah) and the US Public Health Service. Connecticut had no MAC for ammonia, but for the other 5 states and for the USPHS the MAC was 100 ppm. Cook cited Lehmann [91] as the original source published in 1886. Lehmann [91] concluded that 300-500 ppm, following a period of adaptation, could be tolerated for a prolonged period without harm, and further, that concentrations of 1,000-2,000 ppm were safe for short periods. Lehmann recommended that prolonged exposure to concentrations over 500 ppm should definitely not be allowed. Ammonia concentrations of 70-110 ppm in a gas works were said to be at the threshold of irritation.

In 1946, the American Conference of Governmental Industrial Hygienists (ACGIH) established a MAC for ammonia of 100 ppm, [92] which in 1948 became a Threshold Limit Value (TLV), [93] still at 100 ppm. The documentation [94] published in 1962 cited Smyth, [14] Vigliani and Zurlo, [43] Cook, [90] Elkins, [95] and others in support of the 100 ppm TLV. The following year, however, the TLV was reduced to 50 ppm. [96] The 1966 documentation [97] of the 50 ppm TLV cited the reports by Weatherby [49] and Dalhamn [55] in addition to the literature previously cited [94] in support of the 100 ppm TLV. The 50 ppm TLV was said [97] to have been selected to protect against respiratory irritation and was expected to eliminate most complaints of discomfort. In 1969, the ACGIH issued a notice of intent to change the recommended limit of 50 ppm from a time-weighted average (TWA) to a ceiling value. [98] However, the actual change never occurred because the ACGIH recommended in 1970 [99] and adopted in 1973 [100] a TLV of 25 ppm as a TWA. The 1971 documentation [101] stated that experience indicated a "maximum acceptable concentration without severe complaints of 20-25 ppm." This apparently was based on results of unpublished plant surveys conducted by the Detroit Department of Health. The limit of 25 ppm was said to have been selected to protect against eye and respiratory irritation and to "minimize widespread complaints of discomfort among office workers and similar uninured individuals." [101]

The US Navy in 1962 [102] established 25 ppm as the maximum limit for continuous exposure during a 60-day dive in a submarine, and 400 ppm as the maximum allowable concentration permissible for 1 hour under operational conditions.

A number of occupational limits have been set by foreign countries and international groups. The USSR [103,104] established 0.02 mg/liter (approximately 30 ppm) as the workroom air standard. A Spanish standard [105] specified 100 ppm as the "maximum tolerable concentration." After comparison of the ACGIH and USSR recommendations current at the time, the Joint ILO/WHO Committee on Occupational Health [106] in 1968 recommended a safe concentration zone of 20-35 mg/cu m (approximately 30-50 ppm). Included in the ILO/WHO report were MAC recommendations from 12 countries and from 5 states in the United States, with values ranging from 20-70 mg/cu m (30-100 ppm).

The present federal standard (29 CFR 1910.93) for ammonia is an 8-hour time-weighted average of 50 ppm based on the ACGIH recommendation in 1968.

Basis for Recommended Environmental Standard

Exposure to high concentrations of ammonia gas can be fatal, the LC50 for mice, rabbits, and cats having been reported as approximately 10,000 ppm. [46,47] Humans have been killed after accidental exposures to high ammonia concentrations. [17,18,21,27] Because these were accidental exposures ammonia in air was not measured, but in one case [21] a rough estimate of 10,000 ppm was made. Chronic lung disease has been reported after accidental exposure to high concentrations of ammonia gas, [17,19,24,26] and after workers were sprayed or splashed with anhydrous or aqua ammonia. [20,27] As a result of ammonia splashes in the face, permanent eye damage with visual impairment was described in 7 individuals. [20,23,25,28,29] Ammonia gas produced blindness in some guinea pigs exposed for 30-120 minutes at a concentration of 5,000-6,000 ppm. [45]

Guinea pigs exposed at 170 ppm for 6 hours daily, 5 days a week for 18 weeks reportedly developed mild degenerative and congestive changes in the spleens, livers, kidneys, and suprarenal glands. [48] These findings were not duplicated when guinea pigs, rabbits, dogs, and monkeys were exposed at approximately 1,100 ppm for 8 hours daily, 5 days a week for 6 weeks, [50] but nonspecific inflammatory changes were seen in the lungs. There were no abnormal pathological findings [50] in a similar group of animals exposed for the same duration at 220 ppm, at 60 ppm continuously for 114 days, or in rats continuously exposed at 180 ppm for 90 days. Autopsy findings were normal in pigs continuously exposed at concentrations up to 145 ppm for 5 weeks, [51] but Doig and Willoughby [52] reported thickened tracheal epithelium and a decreased number of goblet cells in weanling pigs continuously exposed at approximately 100 ppm for up to 6 weeks. Ammonia has been reported to arrest ciliary activity in rats and rabbits, [54-58] but recovery took place soon after exposure ended. [55] Approximately 100 ppm in the trachea was the lowest concentration that affected the ciliary activity of rabbits. [56,57] The air concentration necessary to reach such a level in the human trachea apparently would be considerably higher, since Landahl and Hermann [36] reported approximately 83% nasal retention in 4 subjects tested. Humans exposed at 500 ppm for 30 minutes [35] and for 4 hours [32] experienced no apparent adverse effects, such as coughing or irritation of the lower respiratory tract, but there was severe upper respiratory irritation and a marked increase in respiratory minute volume. [35] However, particulates might potentiate the effect of ammonia on the lower respiratory tract, since Dalhamn and Reid [58] reported significantly more tracheal damage in rats inhaling ammonia plus activated carbon particles than in rats inhaling either alone.

In a series [38] of 5-minute exposures, 1 of 10 subjects complained of "chest irritation" during exposure at 134 ppm, 5 experienced lacrimation and/or eye irritation, 7 had nasal irritation, and 8 had throat irritation. At 72 ppm, 3 subjects reported eye and throat irritation and 2 experienced nasal irritation. At 50 ppm, 2 of the people reported dryness of the nose, and 1 reported the nasal dryness at 32 ppm. [38] In a second experimental exposure study (Table XI-3), [37] 4 of 6 volunteers exposed at 50 ppm for 10 minutes rated the irritation, on a scale of 0-4, as 2 ("moderate irritation") with the other 2 subjects rating the irritation as 0 ("not detectable") and 1 ("just perceptible"). The irritation at 30 ppm was rated as "not detectable" by 3 of 5 and "just perceptible" by 2 of 5.

No data were found on concentrations that are irritating to workers who are regularly exposed to ammonia and who therefore presumably have a higher irritation threshold. In several of the plant surveys reviewed by Pagnotto, [written communication, September 1973] ammonia concentrations of 9-45 ppm were detected in areas where the industrial hygienist commented that ammonia was initially irritating to the eyes or nose, but that one quickly became accustomed to the ammonia. This phenomenon of acclimatization or inurement was also observed in several experimental exposures, wherein animals appeared to become accustomed to concentrations which initially had been irritating. [50-52]

Other than sensory effects--either irritation or annoyance--there is no evidence of acute or chronic adverse effects of ammonia exposure except after accidental exposure at extremely high concentrations, estimated in one fatal exposure to have been 10,000 ppm. [21] Subjects have been experimentally exposed [32,35] at a concentration of 500 ppm for up to 4 hours. The most serious effect reported, after a 30-minute exposure, was upper respiratory irritation which in 2 of 7 subjects was severe and persisted for 24 hours. [35] At more reasonable concentrations, 100 ppm or less, some individuals report irritation of the eyes and upper respiratory system, and some persons apparently can feel irritation or annoyance even at concentrations below 30 ppm. [37,38,44, and LD Pagnotto, written communication, September 1973]

It is difficult to interpret these subjective reports of irritation at relatively low concentrations of ammonia, since the sensation considered irritating by one individual might be considered merely annoying or disagreeable by another. The term "irritation" obviously is not well defined, as illustrated by the fact that in one experimental exposure, [37] 4 of 6 subjects exposed for 10 minutes considered 50 ppm disagreeable (termed "moderately irritating," Table XI-3), while in another study [38] in which 10 subjects were exposed for 5 minutes, none reported irritation at 50 ppm (2 reported dryness of the nose). At 72 ppm, only 3 reported eye irritation and only 2 reported nasal irritation. [38] This report suggests that most uninured workers might find concentrations as high as 75 ppm not to be irritating in 5 minutes, while the other study [37] suggests that after 10 minutes 50 ppm may become irritating to some. However, other reports of animal [50-52] and human [LD Pagnotto, written communication, September 1973] exposures suggest that one can quickly become accustomed to concentrations of ammonia that at first had been disagreeable.

Although the nasal dryness reported at 50 ppm during a 5-minute exposure [38] might become irritating after extended exposure, the concentration of ammonia inhaled appears to be the more important factor, the irritating or annoying effects being more dependent upon concentration than length of exposure. For this reason, a standard expressed as a time-weighted average is inappropriate since it would permit fluctuations to concentrations considerably higher than 50 ppm. Therefore, in order to minimize the discomfort felt by some unacclimatized individuals, to restrict the potential for fluctuations to more irritating concentrations, and to ensure that such possibly irritating exposures are brief, NIOSH recommends 50 ppm as the environmental standard, expressed as a ceiling not to be exceeded during the workday.

It is recognized that many workers handle small amounts of ammonia or work in situations where, regardless of the amounts used, there is only negligible contact with the substance. Under these conditions, it should not be necessary to comply with all of the provisions of this recommended standard. However, concern for worker health requires that protective measures be instituted below the enforceable limit to ensure that exposures stay below that limit. Therefore, environmental monitoring and recordkeeping is recommended for those work situations which involve exposure above half the recommended limit, to delineate work areas that do not require the expenditure of health resources for control of inhalation hazards. Half the environmental limit has been chosen on the basis of professional judgment rather than on quantitative data that delineate nonhazardous areas from areas in which a hazard definitely exists. Because possibly disabling eye, skin, or respiratory tract injuries may result from accidental exposures, it is recommended that appropriate work practices, training, and other protective measures be required regardless of air concentrations in workplaces with reasonable potential for emergencies. For the same reasons, it is recommended that medical surveillance be made available to anyone adversely affected by ammonia exposure.

It appears that a standard of 50 ppm, expressed as a ceiling, will protect the worker from all adverse effects of long-term ammonia exposure, but epidemiological and experimental studies are needed for verification.

Apparently because of the excellent warning properties of ammonia and the general belief that workers will not remain in acutely hazardous concentrations, there has been little attention to the possibility of effects due to chronic low-level exposure. One study [40] of a small worker population, for whom no exposure data were given, reported no adverse effects on ventilatory function or respiratory symptomatology as a result of exposure to ammonia in an Egyptian ice plant. Another report [41] implicated ammonia as an occupational carcinogen in a group of chemical workers. However, the paper presents insufficient information on the work population, on the exposures involved, and on methods used in the study. The conclusions are therefore unconvincing in the absence of confirmation. These 2 reports [40,41] apparently are the only published attempts to identify chronic effects, if any, of long-term exposure to ammonia. The lack of data on the subject is sufficient to warrant new studies, but the need is made more pressing by the suggestion, despite the weaknesses of the report, that ammonia may be an occupational carcinogen.

VI. WORK PRACTICES

Work practices with regard to the safety precautions for handling anhydrous ammonia are the subject of a considerable body of literature. [2,8,9,88,107-113] Less has been written concerning the use of aqueous solutions of ammonia, [1,114-116] although the problems and effects are essentially similar to those of anhydrous ammonia gas. [1,114] All of these references are concerned largely with prevention and control of hazards arising from emergency situations involving escape of anhydrous ammonia in liquid or gaseous form, or spills of aqua ammonia. The use of natural and/or local exhaust ventilation for control of ammonia gas has had limited review. [2,107,110] Reports of work practices specifically for the prevention of low level exposure are not available. In general, good engineering practices should be used to control continuous low-level exposures and to minimize excursions. For example, good ventilation practices are recommended in the current edition of Industrial Ventilation-A Manual of Recommended Practice published by the American Conference of Governmental Industrial Hygienists.

A. Warning Properties

Fieldner et al [13] reported that the lowest concentration of ammonia detectable by odor was about 50 ppm. Leonardos et al [15] reported 47 ppm as the lowest concentration consistently identified by all 4 subjects exposed to ammonia. If some subjects identified ammonia at lower concentrations, this was not reported. Saifutdinov [16] reported a threshold for olfactory perception of ammonia of 0.7-0.8 ppm, using unspecified methods recommended by the Committee for Sanitary Protection of the Atmosphere (USSR). The American Industrial Hygiene Association's

Hygenic Guide for ammonia [112] reported that the odor of ammonia is detectable at 1-5 ppm, but no supporting evidence was given. These discrepancies in the reported odor threshold need to be resolved, but it does appear that earlier estimates in the 50 ppm range were too high. Despite uncertainty about the odor threshold, the concept that the annoying properties of ammonia will prevent voluntary exposure to acutely hazardous concentrations is frequently encountered. [1,2,9,107-117]

B. Eye Protection

Ammonia is a severe eye hazard, causing serious injury with extreme rapidity. [25,118] On the basis of all available evidence, eye injuries constitute the most serious hazard from ammonia in terms of possible permanent disability. [25] According to Grant, [118] ammonia penetrates the eye more rapidly than other alkalis. For these reasons, it is of extreme importance that water suitable for flushing ammonia from eyes be readily available whenever the possibility exists of eye contact with ammonia. When ammonia is splashed or sprayed into the eyes, time is the most important consideration [118,119] and the first 10 seconds are critical if blindness is to be prevented. [108] Nothing is better than pure water for irrigation of the eyes [118] and no time should be lost searching for a specific antidote other than water. [119] Eyes affected by ammonia should be flushed with water for at least 15 minutes, forcibly holding open the lids if necessary. Medical attention should be obtained without delay, but not at the expense of thoroughly flushing the eyes. Contact lenses prevent effective eye irrigation and should not be worn around ammonia. Chemical goggles with hooded ventilation openings should be used in addition to face shields if eyes and face are not protected by fullface respiratory protection.

C. Skin Protection

During approval tests of respiratory equipment, Patty [39] observed that 1% (10,000 ppm) was mildly irritating to moist skin. Two percent (20,000 ppm) had a more pronounced action, and concentrations of 3% (30,000 ppm) or greater caused a stinging sensation. He postulated that 3% (30,000 ppm) could produce chemical burns with blistering after exposure for a few minutes. The National Safety Council [111] has carried an apparent error through several revisions. Paragraph 66 [111] states "No one can remain in an atmosphere with a concentration higher than 1.5 or 2% (15,000 or 20,000 ppm) of ammonia for more than 15 minutes without developing skin burns and blisters." Paragraph 89 of the same publication states "Atmospheric ammonia in concentrations above 2000 ppm (0.2%) will burn and blister the skin after a few seconds of exposure." No supporting data were given for either statement. In the light of Patty's observations [39] it appears that the second statement is erroneous. Other publications [1,2,9] echo Patty's figures. Therefore, skin protection should be worn in air concentrations of 10,000 ppm or more or when direct skin contact with anhydrous or strong aqua ammonia may occur.

Entry into unknown concentrations of ammonia in emergencies may cause skin injury, therefore, complete skin protection should be worn if possible. Should the emergency require entry without skin protection, stay time should be as brief as possible. Clothing should be removed and a shower taken immediately after leaving the exposure area.

D. Storage and Spills

Theoretical studies [5] and accidents [26,120] indicate that extremely hazardous concentrations of ammonia can exist for considerable distances downwind of liquid anhydrous ammonia spills. Ball [5] calculated the initial "flash," ie, immediate evaporation, from liquid to gas that would result after a spill of liquid anhydrous ammonia. In the case of a pressure-storage system under 126 pounds per square inch gauge (psig) pressure and at 75 F, about 20% of the spill would flash, while only 0.2% would flash after a spill from a refrigerated tank operating at 0.5 psig. In addition, he calculated that, under steady-state conditions of evaporation, ammonia concentrations of 1,000 ppm could exist downwind at a distance of 10 pool diameters with a wind speed of 5 miles per hour (mph). At 25 mph wind speed, 1,000 ppm would be found at a distance of about 4 pool diameters. Calculations were based on square pools of liquid anhydrous ammonia ranging from 30 ft x 30 ft-500 ft x 500 ft. With an atmospheric inversion (conditions which inhibit upward dispersion of the ammonia), these distances could increase between 2-3 times, while an atmospheric lapse state, that is, a condition which does not inhibit upward movement, would substantially reduce the downwind drift.

In a test spill, [121] 1 ton of liquid anhydrous ammonia from a refrigerated atmospheric pressure storage tank was poured into a 5 ft x 22 ft pool. With winds gusting to 15 mph, concentrations of 1,000 ppm or more were detected up to a distance of 150 feet downwind, and concentrations of 50-1,000 ppm were detected up to 500 feet downwind. Ball [5] referred to these results and considered that they correlated reasonably well with his theoretical results when extrapolated to steady-state conditions. Cato and

Dobbs [120] estimated that lethal concentrations existed 100-200 ft from the point of ammonia discharge in a tank car accident. The air temperature was 6-7 F (-17 to -14 C), a gentle breeze was blowing at 3-5 mph, and a temperature inversion existed. Storage areas and containers of ammonia should be located with due consideration of the potential for dispersion and should meet the requirements of 29 CFR 1910.111, as amended.

E. Unusual Sources

Concentrations of ammonia exceeding the recommended limit may originate from unsuspected sources, such as decomposition of organic material in chicken houses, [85] hydrolysis of cyanide emitted from electroplating solutions, [95] and the thermal decomposition of plastics. [122] Personnel should report any unaccounted for ammoniacal odor to responsible supervisory personnel for further investigation.

F. Training

Federal Occupational Safety and Health Standards, 29 CFR 1910.111, state that personnel required to handle ammonia should be trained in safe operating practices and in the proper action to take in the event of emergencies. It further states that employers shall ensure that ammonia unloading operations are performed by properly instructed persons. 29 CFR 1910.134 requires training in the use of respiratory protection. Other references [1,2,107,111,120] stress the importance of training and drills for emergency situations. Accordingly, a requirement for training and drills is recommended.

G. Respirators

Canisters used with respirators have limitations. In ammonia concentrations of 3% by volume (30,000 ppm), an ammonia canister will last for approximately 15 minutes. [107] Canister respirators do not protect in atmospheres deficient in oxygen. Because emergencies involve exposures to unknown concentrations of ammonia, canister type respirators are suitable for outdoor emergency use only. Self-contained breathing apparatus should be used in all other cases. If the odor of ammonia is noticeable while wearing a canister type gas mask, the ammonia concentration is too high for safety, or the canister is not effective. Shelf life of unopened canisters is limited, and unless the manufacturer recommends a shorter period, they should be replaced after 3 years. Used canisters should be promptly replaced.

H. Fire and explosion hazards

While not considered to be a serious fire or explosion hazard, [9] ammonia will burn or explode under some conditions, such as a large and intense source of ignition and a high concentration of ammonia gas. [111] In one experiment, [121] 10 tons of liquid anhydrous ammonia from a refrigerated atmospheric pressure storage tank were pumped into a pit 1 foot deep and 22 feet square. Winds were gusting to 15 mph and the air temperature was 67-70 F. Ammonia gas could not be ignited with small propane torches or with a spark igniter. Oil soaked torches thrown into the pool and into the gas downwind also failed to ignite the ammonia. However, when water was sprayed into the pool of ammonia, the gas ignited and burned on the surface of the pool, moving back and forth with the water streams. The flames died immediately when the water flow was discontinued.

The presence of iron appreciably decreases the ignition temperature, [111] and the presence of oil [2,111] or a mixture of ammonia with other flammable substances increases the fire hazard. [2] Increasing the oxygen content of the air, or increasing the temperature and pressure of the ammonia broadens the flammable (explosive) range. [2] Contact with other chemicals such as mercury, silver oxide, halogens, calcium, and hypochlorite can cause spontaneous explosions due to chemical reactions. [2] Storage areas should be free of oil, oxidizers, or other flammable material. [110] Welding in or on confined spaces such as tanks should only be performed by qualified welders after the space has been thoroughly purged of ammonia. [111]

I. Materials

Moist ammonia corrodes copper, tin, zinc, and many alloys, particularly copper alloys. [2,9,110,111] Therefore, only iron or steel, despite the fact they decrease the ignition temperature, or other nonreactive material should be used in contact with ammonia.

J. Agricultural Uses

With over 80% of the ammonia manufactured being used as fertilizer or in fertilizer manufacture, [5] the potential for accidents involving use of ammonia in agricultural operations is evident. Most reported accidents involve ammonia transfer operations or connecting or disconnecting transfer systems. [25,88] Organizations such as the Fertilizer Institute [123] and the National Society for the Prevention of Blindness Inc [124] publish and distribute material for education and training of personnel in agricultural handling of ammonia. The use of eye, skin, and respiratory protection, and a source of water for immediate washing of skin and eyes are stressed, [108,123] as is training in the handling of ammonia equipment. Water carried on farm vehicles should be protected from freezing by insulation or by an external source of heat. Antifreeze chemicals must not be used. A means of applying the water to the skin and/or eyes in large quantities must be available. The container should have an opening large enough for easy access, should be covered to prevent entry of dirt, and should hold at least 5 gallons. A plastic squeeze bottle containing at least 8 ounces of water should be carried by each individual to allow immediate irrigation of the eyes. This may provide a few additional seconds in which to reach the larger container of water before irreversible eye damage results.

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VIII. APPENDIX I

METHOD FOR SAMPLING AMMONIA IN AIR

General Requirements

Ammonia concentrations shall be determined within the worker's breathing zone and shall meet the following criteria in order to evaluate conformance with the recommended standard:

(a) Samples collected shall be representative of the individual worker's exposure.

(b) Sampling data sheets shall include a log of

(1) The date and time of sample collection

(2) Sampling duration

(3) Volumetric flowrate of sampling

(4) A description of the sampling location

(5) Other pertinent information

Equipment for Air Sampling

(a) Stopwatch

(b) Vacuum pumps with calibrated rotameter

(c) Midget impingers

(d) Solid Standard Taper 24/40 stoppers

(e) Polyvinyl tubing

(f) Dispensing glassware and supporting equipment as may be deemed necessary. Glassware should be borosilicate quality, washed thoroughly with detergent, and followed by rinses with tap water and distilled water.

Reagents

Cautiously add 56 ml of concentrated reagent grade sulfuric acid to 500 ml of distilled water; dilute to 1 liter to obtain 2 N sulfuric acid. Cool to room temperature and dilute 50 ml of the 2 N sulfuric acid to 1 liter with distilled water to obtain 0.1 N sulfuric acid absorbing solution.

Breathing Zone Sampling

Breathing zone samples shall be collected as near as practicable to the worker's face without interfering with his freedom of movement and shall characterize the exposure from each job or specific operation in each production area.

(a) Sampling Equipment

A calibrated personal sampling pump with flowmeter (range up to 2 liters a minute), a midget impinger containing 10 ml of 0.1 N sulfuric acid absorbing solution.

(b) Sampling Procedure

The impinger outlet is connected to the personal sampling pump inlet by a piece of tubing of convenient length, but not in excess of 3 feet. The impinger assembly is attached to the worker's clothing in order to sample from the worker's breathing zone. The sample is collected at a rate of 1 liter a minute for 5 minutes.

A minimum of 3 samples shall be taken for each operation (more samples if the concentrations are close to the recommended standard). At least one blank impinger shall be provided containing sulfuric acid absorbing solution through which no air has been sampled. One additional blank impinger shall be supplied with every 10 samples obtained.

Shipping

After sampling, remove the glass stopper and impinger stem from the impinger bottle. Tap the stem gently against the inside wall of the impinger bottle to recover as much of the sampling solution as possible. Wash the stem with a small amount of unused absorbing solution from a wash bottle, adding the wash to the impinger to bring to a final volume of 20 ml. Stopper the impinger tightly with plastic caps (do not seal with rubber), place in an upright position, and ship the impinger samples to the analytical laboratory in a suitable container to prevent damage in transit. Special impinger shipping containers designed by NIOSH are available. Be certain that the impinger bottles are sealed very tightly to prevent leakage and loss of samples.

Calibration of Sampling Trains

Since the accuracy of an analysis can be no greater than the accuracy of the volume of air which is measured, the accurate calibration of a sampling pump is essential to the correct interpretation of the volume indicated. The frequency of calibration is dependent on the use, care, and handling to which the pump is subjected. In addition, pumps should be recalibrated if they have been misused or if they have just been repaired or received from a manufacturer. If the pump receives hard usage, more frequent calibration may be necessary.

Ordinarily, pumps should be calibrated in the laboratory both before they are used in the field and after they have been used to collect a large number of field samples. The accuracy of calibration is dependent on the type of instrument used as a reference. The choice of calibration instrument will depend largely upon where the calibration is to be performed. For laboratory testing, primary standards such as a spirometer or soapbubble meter are recommended, although other standard calibrating instruments such as a wet test meter or dry gas meter can be used. The actual setups will be similar for all instruments.

Instructions for calibration with the soapbubble meter follow. If another calibration device is selected, equivalent procedures should be used. The calibration setup for personal sampling pumps with a midget impinger is shown in Figure XI-1.

(a) Check the voltage of the pump battery with a voltmeter to assure adequate voltage for calibration. Charge the battery if necessary.

(b) Fill the impinger with 10 ml of the absorbing solution.

(c) Assemble the sampling train as shown in Figure XI-1.

(d) Turn the pump on and moisten the inside of the soapbubble meter by immersing the buret in the soap solution and draw bubbles up the inside until they are able to travel the entire buret length without bursting.

(e) Adjust the pump rotameter to provide a flowrate of 1 liter a minute.

(f) Check the water manometer to insure that the pressure drop across the sampling train does not exceed 13 inches of water (approximately 1 inch of mercury).

(g) Start a soapbubble up the buret and, with a stopwatch, measure the time it takes for the bubble to move from one calibration mark to another. For a 1,000-ml buret, a convenient calibration volume is 500 ml.

(h) Repeat the procedure in (g) above at least twice, average the results, and calculate the flowrate by dividing the volume between the preselected marks by the time required for the soapbubble to traverse the distance.

(i) Data for the calibration include the volume measured, elapsed time, pressure drop, air temperature, atmospheric pressure, serial number of the pump, date, and name of the person performing the calibration.

IX. APPENDIX II

METHOD FOR ANALYSIS OF AIR SAMPLES

Equipment

(a) Spectrophotometer

(b) 50-ml beakers

(c) 1 each 1-, 2-, 5-, 10-, 20-ml pipets

(d) 1-cm cuvettes

(e) 1-liter volumetric flasks

Reagents

(a) Nessler Reagent

Dissolve 100 g of mercury (II) iodide and 70 g of potassium iodide in a small quantity of water, and add this mixture slowly, with stirring, to a cool solution (15-20 C) of 160 g sodium hydroxide in 500 ml water. Dilute to 1 liter. Store in rubber-stoppered borosilicate glassware and out of sunlight to maintain reagent stability for periods up to a year under normal laboratory conditions.

(b) Ammonium chloride, stock solution (1.0 ml = 1.0 mg ammonia)

Dissolve 3.141 g of ammonium chloride in water and dilute to 1 liter with distilled, ammonia-free water.

(c) Ammonium chloride, standard solution (1.0 ml = 10.0 μg ammonia)

Dilute 10.0 ml of 1.0 mg ammonia/ml stock solution to 1000 ml with distilled, ammonia-free water.

Preparation of Standard Curve

To a series of 50-ml beakers add 25.0, 23.0, 20.0, 17.0, and 13.0 ml of absorbing solution (Appendix I). To these beakers in the same order add 0.0, 2.0, 5.0, 8.0, and 12.0 ml of ammonium chloride standard solution, so that the final volume is 25 ml. Add 2.0 ml of Nessler reagent, mix well, and cover beakers. After 20 minutes the color intensity is measured spectrophotometrically in a 1-cm cell at 425 nm against the reagent blank.

Analysis of Samples

Samples should be analyzed within a week of collection. Transfer an aliquot of the blank and sample solutions to 50-ml beakers. Add absorbing solution to adjust the final volume to 25 ml in each beaker. Add 2.0 ml of Nessler reagent, mix well, and cover beakers. After 20 minutes the color intensity is determined by the same procedure as the standards.

Calculations

From the standard curve determine the micrograms of ammonia in the sample solution aliquot. Calculate the concentration of ammonia in the air as ppm:

$$\text{ppm ammonia} = \frac{1.44\ \mu l\ NH3}{\mu g\ NH3} \times \frac{AB}{CDE}$$

Where $$\frac{1.44\ \mu l\ NH3}{\mu g\ NH3} = \frac{\mu mole}{17\ \mu g\ NH3} \times \frac{22.4\ \mu l}{\mu mole} \times \frac{298\ K}{273\ K}$$

A = Sample solution volume in milliliters = 20 ml

(10 ml scrubber solution plus 10 ml rinse)

B = μg of ammonia in aliquot analyzed

C = Volume of aliquot in milliliters

D = Time of sampling period in minutes

E = Sampling impinger flow rate in liters/min.

X. APPENDIX III

MATERIAL SAFETY DATA SHEET

The following items of information which are applicable to a specific product or material containing ammonia shall be provided in the appropriate section of the Material Safety Data Sheet or other approved form. If a specific item of information is inapplicable (eg, flash point), the initials "na" (not applicable) should be inserted.

(a) Section I. Source and Nomenclature.

(1) The name, address, and telephone number of the manufacturer or supplier of the product.

(2) The trade name and synonyms for a mixture of chemicals, a basic structural material, or for a process material; and the trade name and synonyms, chemical name and synonyms, chemical family, and formula for a single chemical.

(b) Section II. Hazardous Ingredients.

(1) Chemical or widely recognized common name of all hazardous ingredients.

(2) The approximate percentage by weight or volume (indicate basis) which each hazardous ingredient of the mixture bears to the whole mixture. This may be indicated as a range or maximum amount, eg, 10-20% V; 10% max. W.

(3) Basis for toxicity for each hazardous material such as an established standard, in appropriate units.

(c) Section III. Physical Data.

Physical properties of the total product including boiling point and melting point in degrees Fahrenheit; vapor pressure, in millimeters of mercury, vapor density of gas or vapor (air = 1), solubility in water in parts per hundred parts of water by weight; specific gravity (water = 1); percent volatile, indicate if by weight or volume, at 70 Fahrenheit; evaporation rate for liquids (indicate whether butyl acetate or ether = 1); and appearance and odor.

(d) Section IV. Fire and Explosion Hazard Data.

Fire and explosion hazard data about a single chemical or a mixture of chemicals, including flash point, in degrees Fahrenheit; flammable limits, in percent by volume in air; suitable extinguishing media or agents; special fire fighting procedures; and unusual fire and explosion hazard information.

(e) Section V. Health Hazard Data.

Toxic level for total compound or mixture, effects of exposure, and emergency and first aid procedures.

(f) Section VI. Reactivity Data.

Chemical stability, incompatibility, hazardous decomposition products, and hazardous polymerization.

(g) Section VII. Spill or Leak Procedures.

Detailed procedures to be followed with emphasis on precautions to be taken in cleaning up and safe disposal of materials leaked or spilled. This includes proper labeling and disposal of containers containing residues, contaminated absorbants, etc.

(h) Section VIII. Special Protection Information.

Requirements for personal protective equipment, such as respirators, eye protection and protective clothing, and ventilation such as local exhaust (at site of product use or application), general, or other special types.

(i) Section IX. Special Precautions.

Any other general precautionary information.

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

Form Approved
OMB No. 44-R1387

MATERIAL SAFETY DATA SHEET

Required under USDL Safety and Health Regulations for Ship Repairing, Shipbuilding, and Shipbreaking (29 CFR 1915, 1916, 1917)

SECTION I

MANUFACTURER'S NAME		EMERGENCY TELEPHONE NO.
ADDRESS *(Number, Street, City, State, and ZIP Code)*		
CHEMICAL NAME AND SYNONYMS		TRADE NAME AND SYNONYMS
CHEMICAL FAMILY	FORMULA	

SECTION II - HAZARDOUS INGREDIENTS

PAINTS, PRESERVATIVES, & SOLVENTS	%	TLV (Units)	ALLOYS AND METALLIC COATINGS	%	TLV (Units)
PIGMENTS			BASE METAL		
CATALYST			ALLOYS		
VEHICLE			METALLIC COATINGS		
SOLVENTS			FILLER METAL PLUS COATING OR CORE FLUX		
ADDITIVES			OTHERS		
OTHERS					

HAZARDOUS MIXTURES OF OTHER LIQUIDS, SOLIDS, OR GASES	%	TLV (Units)

SECTION III - PHYSICAL DATA

BOILING POINT (°F.)		SPECIFIC GRAVITY (H_2O=1)	
VAPOR PRESSURE (mm Hg.)		PERCENT, VOLATILE BY VOLUME (%)	
VAPOR DENSITY (AIR=1)		EVAPORATION RATE (_________ =1)	
SOLUBILITY IN WATER			
APPEARANCE AND ODOR			

SECTION IV - FIRE AND EXPLOSION HAZARD DATA

FLASH POINT (Method used)	FLAMMABLE LIMITS	Lel	Uel
EXTINGUISHING MEDIA			
SPECIAL FIRE FIGHTING PROCEDURES			
UNUSUAL FIRE AND EXPLOSION HAZARDS			

SECTION V - HEALTH HAZARD DATA

THRESHOLD LIMIT VALUE

EFFECTS OF OVEREXPOSURE

EMERGENCY AND FIRST AID PROCEDURES

SECTION VI - REACTIVITY DATA

STABILITY	UNSTABLE		CONDITIONS TO AVOID
	STABLE		

INCOMPATABILITY *(Materials to avoid)*

HAZARDOUS DECOMPOSITION PRODUCTS

HAZARDOUS POLYMERIZATION	MAY OCCUR		CONDITIONS TO AVOID
	WILL NOT OCCUR		

SECTION VII - SPILL OR LEAK PROCEDURES

STEPS TO BE TAKEN IN CASE MATERIAL IS RELEASED OR SPILLED

WASTE DISPOSAL METHOD

SECTION VIII - SPECIAL PROTECTION INFORMATION

RESPIRATORY PROTECTION *(Specify type)*

VENTILATION	LOCAL EXHAUST	SPECIAL
	MECHANICAL *(General)*	OTHER

PROTECTIVE GLOVES	EYE PROTECTION

OTHER PROTECTIVE EQUIPMENT

SECTION IX - SPECIAL PRECAUTIONS

PRECAUTIONS TO BE TAKEN IN HANDLING AND STORING

OTHER PRECAUTIONS

TABLE XI-1

PROPERTIES OF AMMONIA

Property	Anhydrous	Aqua Ammonia (ammonia hydroxide)
Chemical formula	NH_3	NH_4OH
Formula weight	17.03	35.05
Boiling point	-33.35 C	varies with concentration
Melting point	-77.7 C	----
Autoignition temperature	651 C	----
Flammable limits (by volume in air)	16-25%	----
Solubility		
Cold water (0 C)	89.9 g/100 cc	
Hot water (100 C)	7.4 g/100 cc	
Color	Colorless	Colorless

Adapted from references 1-3

TABLE XI-2
OCCUPATIONS WITH POTENTIAL EXPOSURE TO AMMONIA

Acetylene workers
Aluminum workers
Amine workers
Ammonia workers
Ammonium salt makers
Aniline makers
Annealers
Boneblack makers
Braziers
Bronzers
Calcium carbide makers
Case hardeners
Chemical laboratory workers
Chemical manufacturers
Coal tar workers
Coke makers
Color makers
Compressed gas workers
Corn growers
Cyanide makers
Decorators
Diazo reproducing machine operators
Drug makers
Dye intermediate makers
Dye makers
Electroplaters
Electrotypers
Explosive makers
Farmers
Fertilizer workers
Galvanizers
Gas purifiers
Gas workers, illuminating
Glass cleaners
Glue makers
Ice cream makers
Ice makers
Ink makers
Lacquer makers
Latex workers
Maintenance workers (janitors)
Manure handlers
Metal extractors
Metal powder processors
Mirror silverers
Nitric acid makers
Organic chemical synthesizers
Paper makers
Perfume makers
Pesticide makers
Petroleum refinery workers
Photoengravers
Photographic film makers
Plastic cement mixers
Pulp makers
Rayon makers
Refrigeration workers
Resin makers
Rocket fuel makers
Rubber cement mixers
Rubber workers
Salt extractors, coke oven byproducts
Sewer workers
Shellac makers
Shoe finishers
Soda ash makers
Solvay process workers
Stablemen
Steel makers
Sugar refiners
Sulfuric acid workers
Synthetic fiber makers
Tanners
Tannery workers
Textile (cotton) finishers
Transportation workers
Urea makers
Varnish makers
Vulcanizers
Water base paint workers
Water treaters
Wool scourers

Adapted from references 7-9

TABLE XI-3
SUBJECTIVE EVALUATIONS OF IRRITATION AND ODOR

SUBJECT	IRRITATION 30 ppm	IRRITATION 50 ppm	ODOR 30 ppm	ODOR 50 ppm
1	1	2	3	4
2	0	2	4	4
3	0	0	4	4
4	0	1	4	4
5	-	2	-	4
6	1	2	3	4

IRRITANT SCALE (NOSE AND EYE)

DEGREE	INTENSITY	DESCRIPTION
0	No irritation	Not detectable
1	Faint	Just perceptible, not painful
2	Moderate	Moderate irritation
3	Strong	Discomforting, painful, but may be endured
4	Intolerable	Exceedingly painful, cannot be endured

ODOR SCALE

DEGREE	INTENSITY	DESCRIPTION
0	No odor	No detectable odor
1	Very faint	Minimum, but positively perceptible odor
2	Faint	Weak odor, readily perceptible
3	Easily noticeable	Moderate intensity
4	Strong	Highly penetrating
5	Very strong	Intense effect

MacEwen et al [37]

TABLE XI-4

AMMONIA LEVELS FOUND FOR VARIOUS INDUSTRIAL PROCESSES

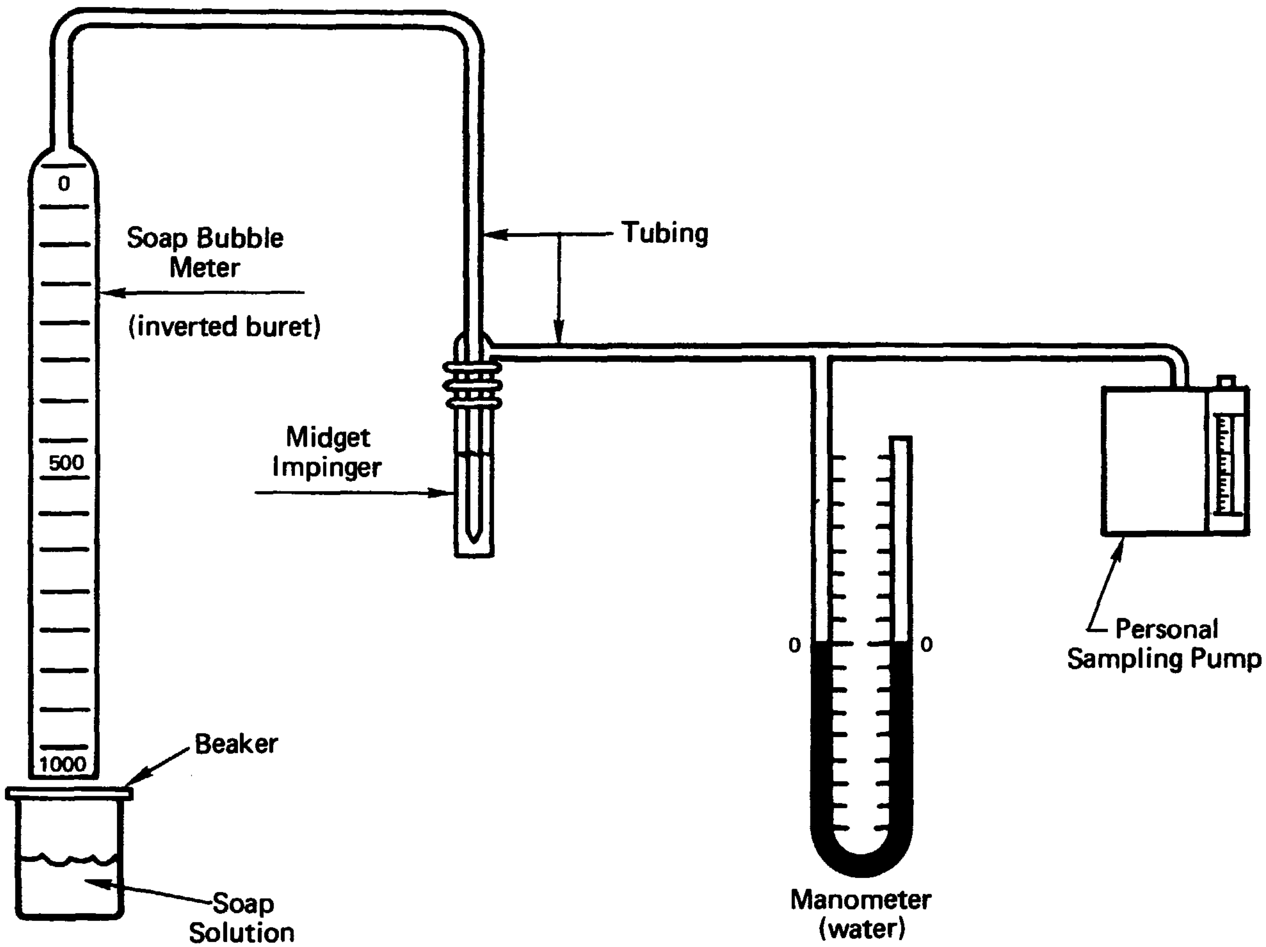
OPERATION	LEVEL	CONTROLS	REMARKS	REFERENCE
Machinery manufacturing (cleaning)	15	Not stated		Rispoli [86]
Diazo reproducing machine	8	Air conditioned room		"
Mildew-proofing	125	Not stated		Elkins [42]
Electroplating	55	"		"
Galvanizing, ammonium chloride flux	10-88	Natural ventilation, monitor roof	Ammonia formed from decomposition of flux	Pate [87]
Blueprint machine	30-35	Not stated		Pagnotto [written communication 1973]
Printing machine	1-45	"		"
Etching	36	"		"
Blueprint machine	10, 20	"		
Refrigeration equipment	9-37	"	Ice cream plant odor noticeable	"
Printing machine	3-29	"	Marked odor, not disagreeable	"
Printing machine	2-45	"		"

TABLE XI-4 (CONTINUED)
AMMONIA LEVELS FOUND FOR VARIOUS INDUSTRIAL PROCESSES

OPERATION	LEVEL	CONTROLS	REMARKS	REFERENCE
Blueprint machine	45	Not stated	Strong odor of ammonia, some eye irritation	Pagnotto [written communication 1973]
Cementing insoles	8-28	"	Latex cement, odor often distinct slight eye irritation	
Chemical mixing	60-440	"	35 gallons of 35% ammonia poured into open trough, intense exposure	"
Fabric impregnating	Not detectable	"		"

FIGURE XI-1

CALIBRATION SETUP FOR PERSONAL SAMPLING PUMP WITH MIDGET IMPINGER



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